



A11103 733806

NISTIR 4649

REFERENCE

NIST
PUBLICATIONS

Data for Fire Hazard Assessment of Selected Non-halogenated and Halogenated Fire Retardants; Report of Test FR 3983

Richard H. Harris, Jr., Vytenis Babrauskas, Barbara C. Levin, and Maya Paabo

NIST United States Department of Commerce
National Institute of Standards and Technology

QC
100
.U56
#4649
1991

NISTIR 4649

NISTR
02100
456
4649
1991

Data for Fire Hazard Assessment of Selected Non-halogenated and Halogenated Fire Retardants; Report of Test FR 3983

Richard H. Harris, Jr., Vytenis Babrauskas, Barbara C. Levin, and Maya Paabo

October 1991



U.S. Department of Commerce
Robert A. Mosbacher, *Secretary*
National Institute of Standards and Technology
John W. Lyons, *Director*
Building and Fire Research Laboratory

Sponsored by:

J. M. Huber Corporation/Solem Division
4940 Peachtree Industrial Blvd.
Norcross, GA 30071

Aluminum Company of America
Alcoa Technical Center
Alcoa Center, PA 15069

TABLE OF CONTENTS

	Page
LIST OF TABLES	iv
LIST OF FIGURES	v
ABSTRACT	1
1. INTRODUCTION	2
2. MATERIALS	3
3. EXPERIMENTAL	4
3.1 Cone Calorimeter	4
3.1.1 Combustion Technique	4
3.1.2 Gas Sampling Through Impingers	5
3.1.3 Test Conditions	5
3.1.4 Data Collected	6
3.1.5 Test Results	6
3.2 Cup Furnace Smoke Toxicity Method	15
3.2.1 Discussion	15
3.2.2 Animals	16
3.2.3 Toxicity Test System	16
3.2.4 Gas Analysis	17
3.2.5 Results	17
4. SUMMARY AND CONCLUSIONS	20
5. ACKNOWLEDGEMENTS	21
6. REFERENCES	23
APPENDIX A. ION CHROMATOGRAPHY PROCEDURE	49

LIST OF TABLES

		Page
Table 1.	Materials Studied	25
Table 2.	Cone Calorimeter Data Summary -- 30 kW/m ² Irradiance Tests without Spark Igniter	26
Table 3.	Cone Calorimeter Data Summary -- Test Average Data at 30 kW/m ² Irradiance without Spark Igniter	28
Table 4.	Cone Calorimeter Data Summary -- 30 kW/m ² Irradiance Tests with Spark Igniter	29
Table 5.	Cone Calorimeter Data Summary -- Test Average Data at 30 kW/m ² Irradiance with Spark Igniter	31
Table 6.	Cone Calorimeter Data Summary -- 100 kW/m ² Irradiance Tests without Spark Igniter	33
Table 7.	Cone Calorimeter Data Summary -- Test Average Data at 100 kW/m ² Irradiance without Spark Igniter	34
Table 8.	Chemical and Toxicological Results from Material 5-VV	35
Table 9.	Chemical and Toxicological Results from Material 6-HH	36
Table 10.	Chemical and Toxicological Results from Material 7-BB	37
Table 11.	Chemical and Toxicological Results from Material 8-EE	38
Table 12.	Chemical and Toxicological Results from Material 11-PP	39
Table 13.	Summary of Chemical and Toxicological Results - Non-flaming	40
Table 14.	Summary of Chemical and Toxicological Results - Flaming	41
Table 15.	Estimated Toxic Potency from High Density Polyethylene with and without Fire Retardants	42

LIST OF FIGURES

	Page
Figure 1. Conceptual view of the Cone Calorimeter	43
Figure 2. Smoke measurement system used on the Cone Calorimeter	44
Figure 3. Impinger gas sampling in the Cone Calorimeter	45
Figure 4. Animal exposure system	46
Figure 5. Post-exposure animal weight change, material 5-VV, 30 min flaming exposure, 39 g/m ³ mass loading	47
Figure 6. Post-exposure animal weight change, material 5-VV, 30 min flaming exposure, 40 g/m ³ mass loading	48

DATA FOR FIRE HAZARD ASSESSMENT OF SELECTED NON-HALOGENATED
AND HALOGENATED FIRE RETARDANTS; REPORT OF TEST 3983

Richard H. Harris, Jr., Vytenis Babrauskas,
Barbara C. Levin, Maya Paabo
Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, Maryland 20899

ABSTRACT

Five plastic materials, with and without fire retardants, were studied to compare the fire hazards of non-halogenated fire retardant additives with halogenated flame retardants. The plastic materials were identified by the sponsors as unsaturated polyesters, thermoplastic high density, low density and cross-linked low density polyethylenes, polypropylene, flexible and rigid poly(vinyl chlorides), and cross-linked and thermoplastic ethylene-vinyl acetate copolymers. The non-halogenated fire retardants tested were aluminum hydroxide ($\text{Al}(\text{OH})_3$), also known as alumina trihydrate (ATH), sodium aluminocarbonate, and magnesium hydroxide. The halogenated flame retardants were chlorine or bromine/antimony oxides. The plastics were studied using the Cone Calorimeter and the cup furnace smoke toxicity method (high density polyethylene only). The Cone Calorimeter provided data on mass consumed, time to ignition, peak rate and peak time of heat release, total heat released, effective heat of combustion, average yields of CO , CO_2 , HCl , and HBr , and average smoke obscuration. The concentrations of toxic gases generated in the cup furnace smoke toxicity method were used to predict the toxic potency of the mixed thermal decomposition products. The data from the Cone Calorimeter indicate that the non-halogenated fire retardants were, in most of the tested plastic formulations, more effective than the halogenated flame retardants in increasing the time to ignition. The non-halogenated fire retardants were also more effective in reducing the mass consumed, peak rate of heat release, total heat released, and effective heat of combustion, and in reducing the amount of smoke produced. The use of halogenated flame retardants increased smoke production and CO yields and, additionally, produced the known acid gases and toxic irritants, HCl and HBr , in measurable quantities. The chemical analytical data for the high density polyethylene samples decomposed via the cup furnace smoke toxicity method in the non-flaming mode indicated that the levels of CO and CO_2 were insufficient to cause death of the test animals (rats), but deaths did occur with all samples except the one containing the halogenated flame retardant. In the flaming mode deaths occurred during exposure to the combustion products from the non-fire retarded control and from the halogenated sample; only in the latter case were the CO and CO_2 concentrations high enough to cause the within exposure deaths. These toxicity results are unusual, but do not indicate a need for concern, since the LC_{50} values are in the range typical of many common materials.

1. INTRODUCTION

Fire retardants are most frequently added to plastics to reduce their ease of ignition. Historically, this has meant increasing a material's resistance to a variety of Bunsen burner type exposures [1]¹. These simple, visual tests have resulted in the modification of many of the most obviously flammable materials, and an accordant increase in fire safety.

In recent years, the fire safety engineers and code officials have perceived a broader concept of product fire safety. This advanced view has caused the examination of other flammability and toxicity characteristics of materials such as:

- Rate of fire growth. This is measured as the rate of heat release from the burning material and the resulting increased temperatures near and away from the fire.
- Smoke obscuration. The time-variant yield of soot and the nature of that soot affect both the spread of alarm and the ability of alerted people to escape.
- Smoke toxicity. Inhalation of the fire products can result in a variety of ill effects ranging from disorientation to death.

This new understanding has led to a more comprehensive way of evaluating the overall fire safety of commercial building and furnishing materials. For fire-retardant (FR) products in particular, the questions have been raised as to 1. does the FR product result in an improved overall fire hazard performance, compared to the non-retarded one; or 2. are there fire performance areas where a particular hazard component is made worse? These are then areas for future improvement.

During the past several years, the National Institute of Standards and Technology's Building and Fire Research Laboratory (NIST-BFRL) (formerly the Center for Fire Research) has been developing the methodology to determine the overall fire hazard of commercial products. This includes the use of advanced bench-scale measurement methods, confirmatory real-scale tests, and computer modeling of fires and their impact [2]. Similarly, in comparing different fire retardants intended for the same application, a fire hazard evaluation should also be performed on each.

J. M. Huber Corporation/Solem Division (SOLEM) and The Aluminum Company of America (ALCOA), manufacturers of alumina trihydrate (ATH) fire and smoke retardants, therefore, asked NIST-BFRL to obtain fire property data for hazard analysis on a series of plastics treated with various FR materials and assess if any of the products posed notable differences from that which could be considered "ordinary". The test materials supplied and identified by the sponsor were in the following categories:

¹ Numbers in brackets refer to literature references listed in Section 6 at the end of this report.

1. not flame retarded;
2. not flame retarded, but filled with inert fillers such as calcium carbonate;
3. flame retarded with ATH;
4. flame retarded with magnesium hydroxide and sodium aluminocarbonate; and
5. flame retarded with halogenated/antimony oxides.

In general, ATH and $Mg(OH)_2$ act as flame retardants and smoke suppressants because of their thermodynamic properties [3,4,5]. Sodium aluminocarbonate is thought to act in the same manner as the ATH and $Mg(OH)_2$, but CO_2 is evolved rather than H_2O . Halogenated flame retardants operate in the vapor phase (interfering with oxidation) and synergize with antimony oxide, also interfering with oxidation [6]. $CaCO_3$ acts as an inert filler thereby reducing the total amount of flammable material.

The plastics were to be studied using the Cone Calorimeter (to monitor rate of heat release, effective heat of combustion, smoke production, and the production of several different gas species) and the cup furnace smoke toxicity method.

The cup furnace smoke toxicity method [7] and the N-gas model [8,9,10,11] were used to evaluate the smoke from burning materials for their toxic potency and any unusual toxic gas generation.

2. MATERIALS

The materials used in the study were provided by SOLEM and ALCOA. They consisted of five plastics, which were generically designated as unsaturated polyester (PES); thermoplastic high density polyethylene (HDPE), low density polyethylene (LDPE), and cross-linked low density polyethylene (XLPE); polypropylene (PP); flexible and rigid poly(vinyl chloride) (F-PVC and R-PVC); and cross-linked and thermoplastic ethylene-vinyl acetate (XL-EVA and TP-EVA). The materials were supplied with and without flame retardants or fillers. The formulations were not verified by NIST-BFRL.

Table 1 is a summary of the materials studied and the amount of flame retarding elements or additives contained therein. With respect to the unsaturated polyesters, there are two sets in the study. Both sets contain 25% glass fiber. In the first set, sample 1-CC is the reference sample. In both sets, the halogen is introduced by a bromine or chlorine substitution on the aromatic ring of the resin. Sample 35 contains nepheline syenite (NPS), an inert filler which is a variety of rock that contains albite and microcline feldspars and nepheline, a mineral with the composition $(Na,K) AlSiO_4$.

Also of note in Table 1 is that the bromine in samples 8-EE, 30-AH, and 15-UU was introduced from a brominated organic additive not specifically identified by the sponsor. The chlorine in samples 31-AJ, 42, and 46 was introduced from Dechlorane Plus (formulation: % weight, Dechlorane Plus 25, antimony oxide 5,

talc 20, Fe compound 0.2, peroxide curing agent 1.4, and antioxidant (1076) 0.7).

The ATH used in the specimens was of a commercial, flame retarded grade of either the ground or precipitated variety [3,12].

There are two sets of rigid poly(vinyl chloride) samples (16 to 18 and 36 to 39). It is not known whether the resin is the same in both sets.

Finally, the flexible PVC samples 19 to 21 all contain 8% clay as well as about 4% of a phthalate ester plasticizer in addition to the other additives listed.

3. EXPERIMENTAL

3.1 Cone Calorimeter

3.1.1 Combustion Technique

The Cone Calorimeter (Figure 1) was initially presented in 1982 as an improved technique for measuring rate of heat release of bench-scale specimens [13]. Its operation involves an application of the oxygen consumption principle. Earlier instruments for measuring rates of heat release were based on either a concept of a well-insulated box, which led to some very serious measurement errors, or on substitution type schemes, which were cumbersome and difficult to operate [14].

The oxygen consumption principle [15] states that for most combustibles there is a unique constant, 13.1 MJ/kg O₂, relating the amount of heat released during a combustion reaction and the amount of oxygen consumed from the air. Thus, using this principle it is only necessary to measure the concentration of oxygen in the flow of the exhaust stream.

In the Cone Calorimeter, specimens of a material or product to be tested are cut into a 100 by 100 mm size. The thickness depends on the type of product tested, and can range from 6 to 50 mm. All specimens, as the final step of specimen preparation, are wrapped in aluminum foil on the bottom and sides to protect the specimen edges from burning. Edge frames and wire grids were used for some of the samples in this test series. The specimen can be oriented either horizontally or vertically. In this test series, all specimens were tested horizontally.

The specimen is irradiated by an electric heater in the shape of a truncated cone, hence the name Cone Calorimeter. The irradiance can be set to any desired value from zero to 110 kW/m². If required, external ignition of the specimen is provided by an electric spark. Since a uniform, controlled irradiance is provided, the ignition times themselves, as measured, constitute a suitable test for ignitability.

The specimen is mounted on a load cell and its mass, along with all other instrument data, is recorded every 5 s.

A few years ago, when shortcomings of existing smoke measuring tests were becoming evident, a smoke measuring system (Figure 2) was evolved for the Cone

Calorimeter. This comprises a He-Ne laser beam projected across the exhaust duct. The monochromatic light is monitored by a solid-state detector. A second detector serves as a reference, to guard against effects of drift and of laser power fluctuations. The optical system is designed to be self-purging, and does not use optical windows. Further details of the smoke measuring system have been given in a recent publication [16].

An overview of the design features, along with the specifications and limitations of the Cone Calorimeter has recently been published [14].

3.1.2 Gas Sampling Through Impingers

Since the Cone Calorimeter represents a well-controlled combustion environment to which specimens can be exposed, it can also be used for the measurement of gaseous species yields. Thus, fixed gas analyzers for O_2 , CO, CO_2 , total hydrocarbons, and H_2O vapor are routinely used. However, it was also necessary to characterize the yields of certain acid gases -- HCl, HBr, and HCN. For these, commercial on-line gas analyzers with a fast enough response time for the Cone Calorimeter test method were not available. Thus a batch sampling technique needed to be employed.

For the batch sampling technique, a portion of the gaseous products and soot in the main exhaust duct of the Cone Calorimeter was collected and analyzed for

HCl, HBr, and HCN by replacing the soot collection filter with a gas sampling apparatus. Figure 3 shows a diagram of the gas sampling apparatus. The gaseous products were collected in tared 125 or 250 mL glass impinger bottles containing approximately 125 mL of 5 mM KOH. A 45 mm diameter PTFE filter (0.45 μm nominal porosity) was placed after the impinger bottle to break the gaseous aerosol and allow maximum collection. The flow of gases through the impinger was controlled by the existing mass flow controller used for soot collection. The ratio of gases collected to gases exhausted was nominally 1:1000; however, the exact value for each test was recorded and used in computations. Sample collection started when the specimen was placed on the load cell of the calorimeter; the collection was stopped when the specimen stopped burning and no more smoke was being evolved.

After the tests were completed, the impinger was weighed and the contents transferred to a plastic container. Before analysis, the filter containing the soot was placed into the solution from the impinger. If HCN was present, the pH of the unknown solutions was determined to make sure that it had not dropped below the pK_a of HCN. The samples were then analyzed for the expected anion(s) by the procedure described in Appendix A.

3.1.3 Test Conditions

The tests were conducted according to the ASTM (American Society for Testing and Materials) method E 1354-90a [17]. To describe fully the test conditions requires specifying not only the specimen orientation (horizontal, face-up) and the use of spark ignition, but also the test irradiance and any special specimen preparation techniques.

Three different irradiance values were used in the test program:

- 10 kW/m² (with spark ignition)
- 30 kW/m² (with and without spark ignition)
- 100 kW/m² (without spark ignition)

The lowest irradiance value, 10 kW/m², would not be expected to cause ignition in most specimens; specimens which are unusually ignition-prone would, however, ignite. The intermediate value, 30 kW/m², represents an irradiative heating value that can readily be imposed by one free-burning item on another. Many bench-scale tests impose heating levels in the range of 30 kW/m² on test specimens. The high value, 100 kW/m², was selected in order to determine if any unusual combustion phenomena become manifest at high irradiances, which are not evident during normal testing. Such high irradiances are typical of the upper ranges of heating values imposed on materials in a fully involved (flashed over) room fire.

3.1.4 Data Collected

The data to be derived from the bench-scale tests in the Cone Calorimeter constitute a very large set, and can be analyzed in a multitude of ways. The most important variables which are presented include the following:

- mass consumed (%),
- time to ignition (s),
- peak rate of heat release (kW/m²) and peak time (s),
- total heat released (MJ/m²),
- average yields of each of the measured gas species (kg/kg),
- average smoke obscuration (m²/kg), and
- effective heat of combustion (MJ/kg).

The effective heat of combustion as determined in the Cone Calorimeter will be less than the oxygen-bomb value of the heat of combustion, since the combustion is incomplete.

In this report we will not be performing any fire hazard evaluations; this is not possible since only bench-scale materials, not full-scale products, were examined. Thus, we will not interpret the test variables to reflect on expected actual fire performance. An example of how such evaluations can be performed once sufficient data are available, is given in [18].

3.1.5 Test Results

The Cone Calorimeter results are summarized in Tables 2 through 7. The values reported, as noted in the sample ID column, are for one test value, or the average of two or three test values. Measures of data uncertainty are thus unknown for all of the specimens. For a discussion of measurement uncertainty see Appendix X2 of [17]. However, for those unsaturated polyester (sample ID

32-35), rigid PVC (sample ID 36), and cross-linked ethylene-vinyl acetate (sample ID 40-43) and thermoplastic ethylene vinyl-acetate (sample ID 44-46) samples run in triplicate, a standard deviation was obtained to determine the repeatability. It should be noted that the runs were not done consecutively for any given set.

Twelve of the specimens which were tested in triplicate were analyzed for repeatability of ignition time, peak rate of heat release, total heat release, effective heat of combustion, and specific smoke extinction area. Although, the data is not formally presented in a table, the following information was obtained. Of the 180 values analyzed, only 6 (3.3%) were outside the 95% confidence limits for repeatability established for the method [17]. Three of the values outside the range were for ignition time, two were for total heat release, and one was for effective heat of combustion. Thus, the repeatability of the data was extremely good for all of the samples that burned to completion.

It should be noted that for the second set of rigid PVC samples (sample ID 36-39), only the reference sample with no FR additive burned to completion in all three replicate tests; at least one sample in each of 37-39 extinguished early in the test and gave questionable data that was not used in the averages reported.

For the 10 kW/m² irradiance, even though the spark igniter was used, none of the three selected HDPE test specimens (5-VV, 7-BB, and 8-EE) ignited. Since the easily ignitable, non-FR HDPE (5-VV) did not ignite at this low flux, none of the other samples were tested at the low flux level. Thus, detailed data at 10 kW/m² were not obtained and no further discussion is made.

At 30 kW/m² irradiance with spark ignition, detailed data for all specimens are presented. For certain specimens, detailed data sets were collected at 30 kW/m² and 100 kW/m² irradiance, both without spark ignition.

The remaining data analysis focuses mainly on the 30 kW/m² results with an occasional reference to the HDPE samples run at 100 kW/m².

In some cases, we will be comparing the various low density polyethylene samples (sample ID 25-27) against sample 5-VV, the HDPE sample containing no additive.

Mass consumed and time to ignition

If the mass consumed of a product is reduced, the resulting toxic potency should also be reduced simply because there is less smoke produced. If the ignition time is delayed, then more time is available for a safe exit from a fire scenario. An effective FR should then reduce the amount of sample consumed in a fire and/or increase the time to ignition.

With respect to the mass consumed data, the percentages listed in Tables 2, 4, and 6 reflect the fact that some of the inert additives and fillers are not consumed. Others, such as the ATH, lose a specific amount of water but also leave a certain amount of residual Al₂O₃. Also to be considered is the

difference in the mass of the chlorine and bromine elements. Therefore, the mass consumed data are strongly influenced by these factors, but should give an indication of the effectiveness of the FR additive.

With respect to sample ignition, at 30 kW/m², only about one half of the samples ignited in the absence of a spark igniter (Table 2), whereas in the presence of a spark igniter, all of the samples ignited at 30 kW/m² irradiance (Table 4).

Details on mass consumed and sample ignition for each resin system are presented in the following discussion.

Without spark ignition

Ignition data for the 30 kW/m² irradiance tests without the spark igniter (Table 2) show that, generally, for those samples that did ignite, the ignition delay times of those specimens containing an additive were increased over the untreated samples.

Specifically, for the unsaturated polyester series, the only sample to ignite was the reference (1-CC) containing the inert filler, CaCO₃, and only about a fourth of the sample was consumed.

In the high density polyethylene series shown in Table 2, the reference (5-VV) ignited and 88% of the sample was consumed. Sample 6-HH with CaCO₃ filler ignited, but lost only about 38% of its weight. There was no ignition of 7-BB which contained ATH and 11-PP which contained Mg(OH)₂. Sample 9-MM with sodium aluminocarbonate lost 48 percent of its weight. Sample 8-EE with the Br/Sb₂O₃ additive had no significant reduction in mass consumed. For those samples that did ignite, the ignition time was increased.

Furthermore, data in Table 6 for the three HDPE samples tested at 100 kW/m², showed that ATH reduced the amount of sample consumed in 7-BB. Ignition times were not changed at this high flux for either additive.

Data in Table 1 indicate that samples 25-AC, 26-AD, and 27-AE, the LDPE, contained increasing amounts of ATH. The mass consumed data in Table 2 at 30 kW/m² show that sample 26-AD, with 50% ATH has more mass consumed than 25-AC with only 45% ATH, probably a reflection of more water being driven off. Sample 27-AE, containing the highest ATH concentration (55 %), did not ignite. Samples 25-AC and 26-AD, with the lower ATH concentrations, ignited, but the ignition times were longer than the reference (sample 5-VV), as previously noted.

The data in Table 2 for samples 28-AF, 29-AG, 30-AH, and 31-AJ, formulated with the XLPE, show that only sample 30-AH containing 10 percent ATH and the Br/Sb₂O₃ additive ignited.

The only sample in the polypropylene series presented in Table 2 that did not ignite was 14-GG with the ATH additive. Both calcium carbonate in 13-FF and Br/Sb₂O₃ in 15-UU resulted in reduced mass consumed, with calcium carbonate more than twice as effective. No ignition time was reported for the calcium

carbonate sample as a result of operator error. The Br/Sb₂O₃ additive increased the ignition time by more than a minute.

With spark ignition

With respect to mass consumed for the tests with the spark igniter (Table 4), replacing the CaCO₃ with other additives in the first set of unsaturated polyester samples (1-CC to 23-II) tended to slightly increase the amount of mass consumed. For the ignition delay, sample 3-XX containing both ATH and Br/Sb₂O₃ increased the ignition time by more than 2 minutes. The ATH in the acrylic-based resin (23-II) increased the ignition time by nearly 2 minutes. The remaining additives only produced small increases in ignition time.

Data in Table 4 for the second set of unsaturated polyesters show that for sample 32 (reference) and 33, formulated with a general purpose resin, the ATH additive in 33 increased the mass consumed by roughly 10% and increased the ignition time by more than two minutes over the inert filler CaCO₃. With respect to the samples formulated with the brominated resin, sample 35 containing ATH and NPS showed a decrease in the mass consumed and more than a minute decrease in the ignition time over sample 34, which had the ATH alone.

The data in Table 4 for the samples in the HDPE series show that all the additives except the Br/Sb₂O₃ in 8-EE reduced the mass consumed and increased the time to ignition. The most effective additive in increasing the ignition time in this set of samples was Mg(OH)₂ (11-PP).

In the LDPE series (25-27), the data in Table 4 indicate that the effect of the increasing ATH concentration on the mass consumed was not significant. Also, the ignition times showed a tendency to decrease instead of increase as might be expected with an increasing ATH concentration. Additionally, the ignition times were slightly less than sample 5-VV which contains no additive.

In the XLPE samples in Table 4, for the samples containing only ATH (28-AF and 29-AG), the increased ATH concentration reduced the mass consumed, but the ignition time was decreased by about a minute. Using a brominated flame retardant in sample 30-AH, as compared to Cl in sample 31-AJ, increased the mass consumed even though the ATH concentration was the same. This was probably a result of the higher formula weight bromine being vaporized. The ignition time was not changed.

In the polypropylene series, the data in Table 4 show that the CaCO₃ additive in 13-FF was the most effective in reducing the mass consumed (a difference ca. 50%); the ATH in 14-GG reduced the mass consumed by roughly 30%. The Br/Sb₂O₃ additive (15-UU) was not effective in reducing the mass consumed. All additives were effective in increasing the ignition time; both the ATH and Br/Sb₂O₃ were equally effective in providing about 70 seconds more ignition time.

The data in Table 4 indicate that the CaCO₃ additive (20) and the ATH additive (21) in the flexible PVC sample only showed a slight reduction in mass consumed and a slight increase in the ignition time (less than 10 seconds with a reference that ignited in 29 seconds).

In the first set of rigid PVC samples (16-19) shown in Table 4, the CaCO_3 additive (17) and the ATH additive (18) decreased the mass consumed by roughly 13 and 10%, respectively. Only the ATH additive was effective in increasing the ignition time by 90 seconds.

In the second set of rigid PVC samples (36-39) shown in Table 4, the ATH in sample 38 was very effective in decreasing the mass consumed; only 18% of the sample was consumed. The $\text{Mg}(\text{OH})_2$ in sample 39 also decreased the mass consumed by more than 30%. Also the ATH and $\text{Mg}(\text{OH})_2$ were very effective in increasing the ignition time (ca. 8 and 3 minutes, respectively.)

All of the additives reduced the mass consumed about 20% in the cross-linked ethylene-vinyl acetate samples shown in Table 4. All of the additives except, the $\text{Cl/Sb}_2\text{O}_3$, increased the ignition time; the ATH in sample 41 nearly doubled the ignition time and the $\text{Mg}(\text{OH})_2$ in sample 43 added more than a minute and a half to the ignition delay.

Finally in Table 4, the ATH in sample 45 of the thermoplastic ethylene-vinyl acetate sample reduced the mass consumed and was more effective in increasing the ignition time than the $\text{Cl/Sb}_2\text{O}_3$ additive in sample 46.

Peak rate of heat release

Without spark ignition

Generally, for the 30 kW/m^2 irradiance tests without the spark igniter (Table 2), the peak rates of heat release (peak \dot{q}'') for those samples that ignited were reduced considerably by the additives. Specifics for each polymer type follow.

Only the reference in the set of unsaturated polyester samples ignited.

For the HDPE samples the peak \dot{q}'' for the control sample (5-VV) was 1760 kW/m^2 . Neither sample 7-BB with ATH additive nor sample 11-PP with $\text{Mg}(\text{OH})_2$ additive ignited in the HDPE set. Sodium aluminocarbonate (9-MM) and CaCO_3 (6-HH) were also very effective in reducing peak \dot{q}'' in the HDPE samples. The least effective additive to the HDPE was the $\text{Br/Sb}_2\text{O}_3$ in sample 8-EE (1280 kW/m^2). Data at 100 kW/m^2 (Table 6) also show the effectiveness of ATH and the brominated flame retardant in reducing the peak \dot{q}'' . At this high flux level, reductions of approximately 2300 and 900 kW/m^2 , respectively, were achieved.

For the three LDPE samples (25-AC, 26-AD, and 27-AE), a tendency for the peak \dot{q}'' to decrease as the ATH concentration increases was observed (sample 27-AE with 55% ATH failed to ignite). The peak \dot{q}'' values for these samples are considerably lower than the reference sample (5-VV).

In the XLPE samples, both samples containing only ATH additive (28-AF and 29-AG) failed to ignite. Sample 31-AJ which contained the chlorinated flame retardant also failed to ignite, whereas 30-AH with the brominated retardant did ignite (peak \dot{q}'' ca. 160 kW/m^2).

Finally, the peak \dot{q}'' of the polypropylene samples was greatly affected by addition of FR additives. The peak \dot{q}'' for the control was 1600 kW/m². Sample 14-GG with ATH failed to ignite. The CaCO₃ in sample 13-FF reduced the peak \dot{q}'' to 25 kW/m² and the Br/Sb₂O₃ additive in 15-UU reduced it to 456 kW/m².

With spark ignition

For the corresponding tests with the spark igniter (Table 4), in general, all of the additives were effective in reducing the peak \dot{q}'' .

For the first set of unsaturated polyester samples (1-CC to 23-II) in Table 4, if 1-CC is used as a reference, then the halogenated resins in conjunction with the Sb₂O₃ were the most effective in reducing the peak \dot{q}'' . Samples 2-QQ and 23-II containing only ATH also decreased the peak \dot{q}'' by 120 to 140 kW/m², respectively.

In the second series of unsaturated polyester samples (32-35) in Table 4, for the general purpose resin, ATH in sample 33 decreased the peak \dot{q}'' by nearly 80 kW/m² in comparison to the CaCO₃ reference (32). For the general purpose, brominated resin set, the reference (34) containing 50% ATH produced a peak \dot{q}'' of 95 kW/m², whereas sample 35 containing only half the amount of ATH in combination with 25% nepheline syenite actually showed a slight increase in the peak \dot{q}'' (118 kW/m²) indicating that the ATH is more effective by itself.

The control (5-VV) for the HDPE samples in Table 4 had a peak \dot{q}'' of 1800 kW/m². None of the other samples, except 8-EE, produced a value greater than 280 kW/m², a truly significant decrease. Sample 7-BB with ATH additive was the most effective in reducing the peak \dot{q}'' . The least effective additive was the Br/Sb₂O₃ in 8-EE. It should be noted from Table 6 for the 100 kW/m² flux tests, that the peak \dot{q}'' of sample 7-BB with ATH also was reduced from about 2600 kW/m² to just over 300 kW/m². Also at 100 kW/m², the Br/Sb₂O₃ additive also reduced the peak \dot{q}'' to just under 1800 kW/m².

In the LDPE series in Table 4, the increased ATH concentration showed a tendency to decrease the peak \dot{q}'' , however, the decrease was small. Again, the peak \dot{q}'' values were considerably less than the reference sample (5-VV).

For the XLPE samples shown in Table 4, the increased ATH concentration in 29-AG versus 28-AF, 55% and 50%, respectively, resulted in a 90 kW/m² decrease in the peak \dot{q}'' ; approximately the same amount of decrease was realized for the sample containing 10% ATH in addition to the Br/Sb₂O₃ (30-AH). The use of chlorine in sample 31-AJ resulted in a much smaller decrease in the peak \dot{q}'' compared to the Br flame retardant in 30-AH.

The peak \dot{q}'' for the reference (12-LL) for the polypropylene samples in Table 4 was nearly 1600 kW/m²; no other sample was over 400 kW/m². This represents a significant decrease for all of the additives. Once again the ATH additive in 14-GG was the most effective in reducing the peak \dot{q}'' .

Both the CaCO₃ in sample 20 and the ATH in sample 21 were effective in reducing the peak \dot{q}'' for the flexible poly(vinyl chloride) samples shown in Table 4. The ATH additive was the most effective with a reduction in peak \dot{q}'' of 120 kW/m².

For the first set of rigid PVC samples shown in Table 4, only the ATH additive in sample 18 was effective in reducing the peak \dot{q}'' . The sample with CaCO_3 (17) actually caused an increase in the peak \dot{q}'' . However, in the second set of rigid PVC samples (36 to 38) shown in Table 4, all of the additives decreased the peak \dot{q}'' by at least 50 kW/m^2 .

The data in Table 4 show that the peak \dot{q}'' was decreased by all of the additives in the cross-linked ethylene-vinyl acetate samples. The control (40) gave a peak \dot{q}'' of 463 kW/m^2 ; the ATH in sample 41 and the $\text{Cl/Sb}_2\text{O}_3$ in sample 42 gave about a 150 kW/m^2 reduction in the peak \dot{q}'' .

Finally, both the ATH and the $\text{Cl/Sb}_2\text{O}_3$ additives in samples 45 and 46, respectively, of the thermoplastic ethylene-vinyl acetate samples shown in Table 4 reduced the peak \dot{q}'' . In this set the ATH reduced the peak \dot{q}'' from almost 600 kW/m^2 for the control (44) to less than 100 kW/m^2 , a substantial decrease. The other additive, $\text{Cl/Sb}_2\text{O}_3$, had more than twice the peak \dot{q}'' of the sample with ATH.

Total heat released

Without spark ignition

The total heat released (total q'') for those samples that contained an additive and ignited in the 30 kW/m^2 irradiance tests without the spark igniter (Table 2) was usually less than their respective reference samples. The column of total q'' data indicates that samples containing ATH, alone or in combination with other additives, were those samples that failed to ignite or gave very low total q'' 's compared to their controls.

Data in Table 6 for the 100 kW/m^2 irradiance also show a reduction in the total q'' by using flame retardants. At the higher irradiance level the brominated flame retardant was more effective than ATH by roughly 30 MJ/m^2 .

With spark ignition

The same pattern of decreased total q'' for samples containing an additive(s) was not seen for all of the polymers in the tests with the spark igniter (Table 4). No reduction in total q'' was achieved by additives in the second series of unsaturated polyester samples, the flexible PVC samples, or the thermoplastic ethylene-vinyl acetate samples. The total q'' for the first set of rigid PVC samples (16-18) was very low ($2\text{-}7 \text{ MJ/m}^2$); the ATH sample (18) in this set gave the 2 MJ/m^2 and both the control (16) and the CaCO_3 additive sample (17) were comparable at 7 MJ/m^2 .

For the first set of unsaturated polyester samples shown in Table 4, samples 3-XX and 4-AA formulated with the halogenated resins were the most effective in reducing the total q'' ; sample 4-AA with Cl was especially effective. Samples 2-QQ and 23-II, containing only ATH, had little effect on reducing the total q'' .

The sample with $\text{Br/Sb}_2\text{O}_3$ (8-EE) in the HDPE series shown in Table 4 was most effective in reducing the total q'' (a difference of 90 MJ/m^2). The sample with ATH (7-BB) was also effective with a 70 MJ/m^2 reduction in the total q'' .

The samples with CaCO₃ (6-HH), sodium aluminocarbonate (9-MM), and Mg(OH)₂ (11-PP) reduced the total q" by roughly 50 MJ/m².

For the LDPE samples (25-27) shown in Table 4 there was no decrease in the total q" with increasing ATH concentration as might be expected. Also, only slight reductions in the total q" are seen for the XLPE samples (28-31.) All of the additives to the polypropylene samples (12-15) shown in Table 4 reduced the total q"; a reduction of 35-42 MJ/m² was achieved.

For the second set of rigid PVC samples shown in Table 4, the ATH additive (38) and the Mg(OH)₂ additive (39) reduced the total q" from 29 MJ/m² for the control (36) to 18 MJ/m². The inert CaCO₃ additive (37) was comparable to the control (36) with respect to total q" (ca. 30 MJ/m²).

Finally in Table 4, for the cross-linked ethylene-vinyl acetate samples (40-43), only a small affect on the total q" was noted. The control (40) gave a total q" of 67 MJ/m². The ATH sample (41) was comparable (62 MJ/m²). The Cl/Sb₂O₃ sample (42) was the most effective in reducing the total q" (39 MJ/m²) and the Mg(OH)₂ sample (43) gave a slight reduction at 53 MJ/m².

Effective heat of combustion

Without spark ignition

Because of the many samples that failed to ignite in the 30 kW/m² irradiance tests without the spark igniter (Table 2), the effective heat of combustion (eff. Δh_c) for those samples that ignited was evaluated only for the high density polyethylene and polypropylene samples. For the HDPE samples, the reference sample (5-VV) gave an eff. Δh_c of 54 MJ/kg. Neither samples 7-BB with ATH nor 11-PP with Mg(OH)₂ ignited. The CaCO₃ in sample 6-HH and the Br/Sb₂O₃ in sample 8-EE were not effective in reducing the eff. Δh_c. A reduction in eff. Δh_c of about 20 MJ/kg was achieved by the sodium aluminocarbonate (9-MM) sample. At the 100 kW/m² flux (Table 6), there was essentially no difference in the eff. Δh_c for this set of samples.

In the polypropylene series, the control (12-LL) produced an eff. Δh_c of 59 MJ/kg. Sample 14-GG with ATH failed to ignite. Also, both the CaCO₃ in sample 13-FF and the Br/Sb₂O₃ in sample 15-UU were effective in reducing the eff. Δh_c (7 and 18 MJ/kg, respectively.)

With spark ignition

For the tests with the spark igniter (Table 4), a reduction in the eff. Δh_c was realized for some of the polymer samples, but not for others. Those polymer samples that were not affected by the addition of additives were the LDPE samples with increasing ATH concentrations (25-27), the flexible PVC (19-21), and both sets of rigid PVC (16-18 and 36-39).

The eff. Δh_c for the reference (1-CC) in the first unsaturated polyester series shown in Table 4 was 22 MJ/kg. The most effective additives in reducing the eff. Δh_c were the halogens in samples 3-XX and 4-AA (12 and 5

MJ/kg, respectively). Both samples containing ATH (2-QQ and 23-II) were only slightly effective in reducing the eff. Δh_c .

In the second series of general purpose polyester resins shown in Table 4, only a small reduction in the eff. Δh_c was found. A 6 MJ/kg reduction in eff. Δh_c resulted from the substitution of ATH (33) for CaCO_3 (32) in the first non-brominated set. No change in the eff. Δh_c for partial substitution of ATH with nepheline syenite in the brominated resin set was seen.

Only sodium aluminocarbonate and ATH additives (9-MM and 7-BB) in the HDPE samples were effective in reducing the eff. Δh_c . The reference sample (5-VV) had an eff. Δh_c of 59 MJ/kg. The eff. Δh_c 's of the aforementioned samples were 31 and 43 MJ/kg, respectively. The other three FR additives were not effective.

In the XLPE set of samples shown in Table 4, only 30-AH with the $\text{Br/Sb}_2\text{O}_3$ /ATH additives showed a reduction in the eff. Δh_c .

The eff. Δh_c for the reference (12-LL) in the polypropylene set was 60 MJ/kg. The only additive in the polypropylene samples to produce a significant reduction in the eff. Δh_c was $\text{Br/Sb}_2\text{O}_3$ in 15-UU, which reduced the eff. Δh_c to 18 MJ/kg. The ATH additive in sample 14-GG reduced the eff. Δh_c to 45 MJ/kg. The inert CaCO_3 additive (13-FF) had no effect on the eff. Δh_c .

The eff. Δh_c for the reference (40) in the cross-linked ethylene-vinyl acetate samples was 31 MJ/kg. The $\text{Cl/Sb}_2\text{O}_3$ additive in sample 46 reduced the eff. Δh_c to 17 MJ/kg. Both the ATH in sample 41 and the Mg(OH)_2 in sample 43 reduced the eff. Δh_c , but by only about 7 MJ/kg.

Finally, the ATH in sample 45 and the $\text{Cl/Sb}_2\text{O}_3$ in sample 46 of the thermoplastic EVA gave a small reduction in the eff. Δh_c of about 7 MJ/kg, with the control at 27 MJ/kg.

Average smoke obscuration and average yields of measured gases

Without spark ignition

The data in Table 3 represent CO , CO_2 and smoke generation for the specimens tested at 30 kW/m^2 irradiance without the spark igniter. For most of the samples that ignited, the CO generation was on the order of 0.01-0.03 kg/kg, with a tendency for the samples with halogen additives to be higher. Notably higher CO generation for 30-AH, the XLPE sample with the $\text{Br/Sb}_2\text{O}_3$ /ATH additive and 15-UU, the polypropylene sample with the $\text{Br/Sb}_2\text{O}_3$ additive was seen. Both of these samples gave CO values of 0.15 kg/kg. The corresponding CO_2 values were also lower than most of the other test values. For the other CO_2 values, there was also a tendency for the additives to lower the CO_2 generation. The very low CO_2 value for 13-FF is questionable.

Data at 100 kW/m^2 (Table 7) for the HDPE samples also showed a decrease in CO production with the ATH sample (7-BB) and an increase with the $\text{Br/Sb}_2\text{O}_3$ sample (8-EE), while both additives decreased the CO_2 production.

Also, the smoke generation data at 30 kW/m² irradiance without the spark igniter (Table 3) indicated that halogenated additives increased the smoke produced for those samples that ignited.

However, data in Table 7 for smoke generation at 100 kW/m² for the HDPE samples showed an increase over the control for both the ATH and the Br/Sb₂O₃ additives.

With spark ignition

The data in Table 5 give the quantities of CO, CO₂ and smoke generated at 30 kW/m² irradiance with the spark igniter. Similar to the tests without the spark igniter, the CO increased and the CO₂ decreased when the additive contained a halogen. An increase in the production of CO was also noted for the ATH additive in the HDPE, the second series of rigid PVC, and the thermoplastic EVA. The LDPE samples with increasing ATH concentrations (25-27) also showed an increase in the CO production with increasing ATH concentration. Similar to the tests without the spark igniter, the higher CO production resulted in a lower CO₂ production. Interestingly, in the XLPE sample 30-AH containing Br and ATH as compared to sample 31 with Cl and ATH, about twice the CO production resulted with the Br additive. Also of note was the high CO production of the flexible PVC samples (19-21); the control with no additive produced more than 0.11 kg/kg of CO.

Results similar to those for tests without spark ignition were obtained for smoke generation in the tests with the spark igniter (Table 5). The samples containing Br/Sb₂O₃, Cl/Sb₂O₃, and CaCO₃ produced much more smoke than their respective references. The ATH, sodium aluminum carbonate, and magnesium hydroxide additives were very effective in reducing smoke; samples 26 and 7-BB were the most effective.

In the tests with the spark igniter, for those samples containing a halogenated FR the portion of the combustion products collected in the impingers and analyzed by IC confirmed the presence of the halogen. Since the acid gases are known to be irritants and contribute to post-exposure deaths at concentrations near their LC₅₀, a measure of their production is important. The reported results are based on the calculation of chloride and bromide ion content to the acid gases only. If other halogenated species in the combustion products are contributing to the anion(s), then this value might be in error with respect to acid gas generation.

3.2 Cup Furnace Smoke Toxicity Method

3.2.1 Discussion

For the smoke toxicity portion of this study, the current N-Gas model was used to predict the toxicity of the thermal decomposition products of materials based on experiments at NIST on the mixtures of toxicants. That prediction and evaluation are based on data from earlier NIST experiments on the combined toxicity of the major gases produced in fires. The N-Gas model is designed to determine whether the lethality of the thermal decomposition products of a

material can be explained by the toxicological interaction of these major gases or if other toxic combustion products need to be considered [8,19,20].

The first step in the use of the N-Gas model is the prediction of the LC_{50} values based on the measured concentrations of a predetermined set of gases and knowledge of their toxicological interactions. Experiments with rats were conducted at approximately the predicted LC_{50} value and if the prediction is correct, some of the animals will die. Death of all the animals indicates that other toxic gases need to be included in the model. Currently, five gases, CO, CO₂, HCl, HCN, and reduced O₂ have been examined both individually and in various mixtures and are included in the model [19,20,21]. As more information is obtained, more gases will be added.

In this project, toxicity experiments on a few samples were conducted to test the predictive capabilities of the N-Gas model and to check for the presence of additional unknown toxicants. The high density polyethylene samples containing no additive (5-VV), CaCO₃ (6-HH), ATH (7-BB), Br/Sb₂O₃ (8-EE), and Mg(OH)₂ (11-PP) were examined under both flaming and non-flaming conditions using the cup furnace apparatus [7].

3.2.2 Animals

Fischer 344 male rats, weighing 200-300 grams, were obtained from the Harlan Sprague-Dawley Company² (Walkersville, MD) or from Taconic Farms (Germantown, NY). They were allowed to acclimate to our laboratory conditions for at least 10 days before experimentation. Animal care and maintenance were performed in accordance with the procedures outlined in the National Institutes of Health's "Guide for the Care and Use of Laboratory Animals." Each rat was housed individually in suspended stainless steel cages and provided with food and water ad libitum. Twelve hours of fluorescent lighting per day were provided using an automatic timer. All animals (including the controls) were weighed daily from the day of arrival until the end of the post-exposure observation period.

3.2.3 Toxicity Test System

The acute inhalation toxicity of the combustion products of the above materials was assessed using the combustion system, the chemical analysis system and the animal exposure system that was designed for the cup furnace smoke toxicity method [7]. Analytical experiments without animals were conducted first under both flaming and non-flaming conditions to determine the concentrations of CO, CO₂, and HCN that would be generated from different mass loadings of each material. These values were then used to predict the LC_{50} values which would then be used as the mass of material to be tested in the

²Certain commercial equipment, instruments, materials or companies are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment or material identified is necessarily the best available for the purpose.

animal exposures. If, at the highest mass loading (40 g/m^3) of material permitted by the method, the combined concentrations of these gases were still below the predicted LC_{50} , the animals were tested at 40 g/m^3 .

The animal exposure system (Figure 4) is a closed design in which all the gases and smoke are kept in the 200 liter rectangular chamber for the duration of the experiment. The materials are decomposed in a cup furnace located directly below the animal exposure chamber such that all the combustion products from the test materials are evolved directly into the chamber. The materials are examined under separate non-flaming and flaming conditions which are achieved by setting the furnace 25°C below and above each material's predetermined autoignition temperature.

In the animal exposure experiments, six rats were exposed in each experiment. Animals were placed in restrainers which were then inserted into the six portholes located along the front of the exposure chamber such that only the heads of the animals were exposed. The animals were exposed to the initial generation (usually 5 min) of the test atmosphere as well as the later steady-state conditions. The toxicological endpoint was death which occurred either during the 30 minute exposures or the 14 day post-exposure observation period.

3.2.4 Gas Analysis

Carbon monoxide and CO_2 were measured continuously by non-dispersive infrared analyzers. Oxygen concentrations were measured continuously with either a galvanic cell or a paramagnetic analyzer. Information obtained from SOLEM/ALCOA representatives indicated that these five materials did not contain nitrogen; therefore, analysis of HCN was not conducted. Analysis for HBr in 8-EE was not done either. The CO , CO_2 , and O_2 data were recorded by an on-line computer every 15 seconds. All combustion products and gases that were removed for chemical analysis were returned to the chamber. All given gas concentrations are the average integrated exposure values which were calculated by integrating the area under the instrument response curve and dividing by the exposure time.

3.2.5 Results

The chemical and toxicological data for the materials designated 5-VV, 6-HH, 7-BB, 8-EE, and 11-PP are presented in Tables 8-12, summarized in Tables 13-15, and discussed below.

Material 5-VV

The autoignition temperature was initially determined to be 375°C , and the flaming experiments were therefore performed 25°C above that temperature. The data in Table 8 indicate that no animals died within the 30 minute exposures to the flaming decomposition products from approximately 40 g/m^3 of Material 5-VV. However, following a flaming exposure to 39 g/m^3 , one animal died within 24 hours and the other five animals lost considerable weight (as much as 60 grams over 4 days) before showing signs of recovery (Figure 5). In another flaming experiment at 40 g/m^3 , one animal was sacrificed after losing 140 grams of weight over 39 days, although the other 5 animals appeared to

recover after approximately 3 days (Figure 6). The concentrations of CO and CO₂ were insufficient to account for the death that occurred. However, the presence of one or more additional toxic gases from the decomposition of the polyethylene resin might be responsible for the death.

The non-flaming experiments were performed at two different temperatures - approximately 350°C and 375°C. The temperature was increased after noting the large residue remaining in the cup furnace following the non-flaming experiments at 350°C. The autoignition temperature was rechecked and found to be 25°C higher than that found previously.

At the lower temperature, two experiments at a mass loading of 40 g/m³ did not produce deaths either within or following the exposures. However, when the temperature was increased to 375°C, two animals died during the 30 minute exposure to the combustion products from a mass loading of 39 g/m³. Two died within 4 minutes following the exposure and the remaining two died later that afternoon. At lower mass loadings - 20 and 30 g/m³ - no deaths were observed during the exposures but all the animals died within 24 hours following the exposures. In the non-flaming mode, the deaths that occurred could not be attributed to the concentrations of CO and CO₂ generated, but additional toxic gases might have been produced. Previous studies [22, 23] have shown that oxidative pyrolysis of polyethylene at 300-400 °C produce toxic, low molecular weight organic species such as acrolein and formaldehyde. These compounds are most likely to produce post-exposure deaths.

Material 6-HH

The results from the flaming experiments performed 25°C above the autoignition temperature (450°C) showed that no deaths occurred either during the 30 minute exposures or the post-exposure observation periods (Table 9). In the non-flaming mode, no deaths were observed during the 30 minutes of actual exposure; however, all but one of the animals died 24 to 72 hours following the tests. Based on the concentrations of CO and CO₂ generated when material 6-HH was decomposed in the flaming and non-flaming modes, no deaths were predicted from any of the mass loadings tested. Therefore, the post-exposure deaths that occurred following the non-flaming decomposition of Material 6-HH cannot be attributed to only CO and CO₂, but were probably due to the presence of one or more additional toxic gases that were also produced [22, 23].

Material 7-BB

The flaming experimental results showed that no deaths occurred either during the 30 minute exposures or the post-exposure observation periods (Table 10). In the non-flaming mode, no deaths were observed during the 30 minutes of actual exposure, but deaths did occur 24 to 48 hours following the tests. In one non-flaming experiment, the material started flaming approximately 10 minutes after the start of the test. This was the only case in which one animal died during the 30 minute exposure; another animal died five days later. Based on the concentrations of CO and CO₂ generated when material 7-BB was decomposed in the flaming and non-flaming modes, no deaths would have been predicted to occur from any of the mass loadings tested. The post-exposure deaths that occurred following the non-flaming decomposition of Material 7-BB

were, therefore, not due to the CO and CO₂, but were probably due to the presence of one or more additional toxic gases [22, 23].

Material 8-EE

One animal died within the exposure and five died post-exposure from the flaming decomposition products of Material 8-EE (Table 11). The post-exposure deaths occurred as late as 4 days after the tests. The concentrations of CO and CO₂ were sufficient to account for the deaths that occurred up to 24 hours post-exposure, but would not have accounted for the deaths occurring later. These deaths might have been caused by additional toxic gases. In the non-flaming mode, no deaths were predicted based on the CO and CO₂ concentrations and no deaths occurred.

Material 11-PP

No deaths were observed from the flaming decomposition products from Material 11-PP (Table 12). In the non-flaming mode, there were no deaths during the 30 minute exposures, but many of the animals died following the tests. Most of these deaths occurred during the first three days; however, one animal died as late as 24 days following the exposure. Based on the levels of CO and CO₂, no deaths were expected. The post-exposure deaths from the non-flaming mode are not attributable to the toxicological interactions of CO and CO₂, but are probably due to one or more additional toxic gases [22, 23].

The data from the five tests are summarized in Tables 13-15. The non-flaming test results in Table 13 indicate within and post-exposure deaths for the untreated HDPE at 375°C and mass loadings from 20-39 g/m³. Deaths were also experienced for the samples containing CaCO₃, ATH, and magnesium hydroxide, probably as a result of the same additional toxic gases that are being generated from the control. No deaths were experienced for the sample containing the Br/Sb₂O₃ additive. Since the halogenated flame retardants function in the vapor phase, perhaps the vapor phase reactions also prevent the formation of additional toxic gases, thus reducing within and post-exposure deaths.

The data in Table 14 for the flaming mode indicate that fewer deaths occur for all the samples at a loading of 30-40 g/m³ than in the non-flaming mode. The only additive-containing sample that produced deaths was 8-EE with Br/Sb₂O₃. These deaths were probably a result of the higher CO levels acting in conjunction with the CO₂ [19, 20] along with the added brominated FR.

The toxicological data for both the flaming and non-flaming modes are summarized in Table 15. The data points out the problems that arose from conducting these experiments without any knowledge of the formulations of the materials and the amounts of additives and fillers. To actually determine the degree to which the additives contributed to the toxic potency of the materials, it would be necessary to determine more precise LC₅₀ values based on mass consumed.

4. SUMMARY AND CONCLUSIONS

Full-scale fire behavior can, at the moment, be predicted from bench-scale data only under limited circumstances. To do this, it is required that specific end-use products be identified, and that an appropriate full-scale/bench-scale correlation be available for this product category [18]. Realistic estimates of the production of smoke or toxic gases cannot be made unless either full-scale tests are conducted or such correlations are available. Thus, the results below are indicative only, and are not a quantitative estimate of the full-scale fire hazards involved.

Nonetheless, changes in the key properties measured (ignition delay, rate of heat release, total heat release, and smoke toxic potency) may well be indicators of changes in hazard.

The data obtained from the Cone Calorimeter on a limited number of samples whose formulations were not verified by NIST suggest that in most samples tested, ATH was an effective fire retardant and smoke suppressant when used at levels from 30 to 65% by weight. The samples containing halogen/antimony oxide flame retardants at levels of 2.5 to 15% by weight were also effective fire retardants, but not particularly effective as smoke suppressants. NIST has neither determined whether these are optimal additive levels for fire safety enhancement, nor assessed whether one can extrapolate these results to other loadings.

The following information is noted from the data:

- In the tests at 30 kW/m² without the spark igniter, the samples containing ATH at levels of 50% by weight or greater in all polymer formulations failed to ignite. The two samples containing the chlorine as a flame retardant, without ATH in the PES formulation or in combination with 10% ATH in the XLPE formulation, also failed to ignite. Three of the four polymer formulations containing bromine as the flame retardant ignited (the PES formulation that did not ignite also contained 50% by weight ATH).
- For tests at 30 kW/m² with the spark igniter, the ignition times were longer for samples containing ATH alone, halogenated/antimony oxide flame retardants (with the exception of the HDPE formulation) or ATH in combination with halogenated/antimony oxide flame retardants.
- For tests at 30 kW/m² with the spark igniter, a 15-fold decrease in the peak rate of heat released for the polypropylene formulation was achieved with 57% by weight ATH. A less than 2-fold decrease was achieved with the sample containing Br/Sb₂O₃ (14/6% by weight).
- With respect to smoke yields, a comparison of the same two samples from above shows a more than 7-fold decrease in the smoke generation from a sample with ATH compared to an almost 3-fold increase in smoke from the Br/Sb₂O₃ flame retardant.

- In all samples that contained only a halogenated/antimony oxide FR, the smoke production was increased.
- Also of note was the increase of CO production with the halogenated/antimony oxide FR additives.
- In the HDPE formulation, the sodium aluminocarbonate and magnesium hydroxide were also more effective as fire retardants than the halogen/antimony oxide combinations in increasing ignition time, reducing mass consumed, peak \dot{q}'' , CO production, and smoke generation; they were not as effective as ATH.
- The inert filler, CaCO_3 , was effective in reducing the mass consumed and amount of heat released, but caused an increase in smoke production. In the PVC formulations, the CaCO_3 actually decreased the ignition time.

In the toxic potency testing, only a selected sub-group of five samples of high density polyethylene was examined. In the non-flaming mode, the N-Gas Model used for analysis predicted no deaths based on the CO and CO_2 production for any of the samples. However, deaths (mostly during the post-exposure observation period) did occur with all samples except 8-EE with $\text{Br/Sb}_2\text{O}_3$. These deaths might be a result of other toxic gases not analyzed. Also of note in the non-flaming mode was the much lower production of CO and CO_2 for sample 8-EE.

In the flaming mode, there were two cases in which deaths occurred during or immediately following the 30 minute exposures and they were specimen 5-VV without additive at the highest mass loading - 39 g/m^3 and sample 8-EE with $\text{Br/Sb}_2\text{O}_3$ at a comparable mass loading. In only one case (sample 8-EE) was the predicted concentration of CO and CO_2 high enough to cause within-exposure deaths. Also, samples 5-VV and 8-EE were the only samples to be completely consumed.

In the non-flaming mode, for sample 5-VV, the high density polyethylene without additives, 70 to 85% of the material was consumed when the material was decomposed at $375 \text{ }^\circ\text{C}$; for samples 6-HH, 7-BB and 11-PP only 40 to 60% of the samples were consumed and may be the reason that fewer deaths occurred during the 30 minute flaming exposures. The possibility of deaths at higher mass loadings of material was not examined since the cup furnace smoke toxicity method specifies a maximum mass loading of 40 g/m^3 (materials not toxic at this loading are considered to have a low toxic potency).

The observed deaths, which were not predicted by combined interactions of CO and CO_2 , were probably due to the additional toxic effects of unmeasured gases. However, the predicted toxic potency values all fall into a range typical of many common materials.

5. ACKNOWLEDGEMENTS

The authors thank Dr. Richard G. Gann for his valuable editing and technical advice, Dr. Joshua L. Gurman for his help and advice in setting up the

experiments, and Ms. Helene Clark, Ms. Margaret Yoklavich, Ms. Carmen Davis and Messrs. W. H. Twilley and J. R. Shields for their technical assistance in performing the experiments. Ms. Helene Clarke and Ms. Margaret Yoklavich were guest workers under the auspices of the University of Pittsburgh Graduate School of Public Health, Pittsburgh, PA.

6. REFERENCES

- [1] Test for Flammability of Plastic Materials for Parts in Devices and Appliances, UL 94, Underwriter's Laboratory, Northbrook, Illinois, 1990.
- [2] Bukowski, R. W., Peacock, R. D., Jones, W. W., Forney, C. L., Software User's Guide for the HAZARD I Fire Hazard Assessment, Vol. 1, National Institute of Standards and Technology, NIST HB-146/I, 1989.
- [3] Keating, J. Z., Alumina Trihydrate: Flame-retarding, Smoke-suppressing Filler, **Plastics Compounding**, July/August, 1980.
- [4] Gal, E., Pal, A., Rychly, J., Tarapcikova, K., Mechanism of Aluminum and Magnesium Hydroxide Action in Halogen-Free Fire Retardant Polymer Composites, **Flame Retardants 1990**, International Conference, 1990, Elsevier Applied Science, New York, 134-143 pp, 1990.
- [5] Agnew, A., Aspects of the use of Aluminum Hydroxide as a Fire Retardant Filler for Polymeric Materials, **Fire Retardants: Proceedings of 1978 Conference on Flammability and Fire Retardants**, July 1978, Technomic Publishing Co., Connecticut, Bhatnager, V. M., editor, 1-14 pp, 1978
- [6] Lyons, J. W., **The Chemistry and Uses of Fire Retardants**, p. 14-24, Wiley-Interscience, New York, (1970).
- [7] Levin, B. C., Fowell, A. J., Birky, M. M., Paabo, M., Stolte, A., and Malek, D., Further Development of a Test Method for the Assessment of the Acute Inhalation Toxicity of Combustion Products. NBSIR 82-2532, National Bureau of Standards, Gaithersburg, MD, 1982.
- [8] Levin, B.C. and Gann, R.G.. Toxic Potency of Fire Smoke: Measurement and Use, Fire and Polymers: Hazards Identification and Prevention, Ed. by G.L. Nelson, ACS Symposium Series 425, American Chemical Society, Washington, DC, pp.3-11, 1990.
- [9] Braun, E., Levin, B. C., Paabo, M., Gurman, J., Holt, T., Steel, J. S., Fire Toxicity Scaling (NBSIR 87-3510). [U.S.] Nat. Bur. Stand. (1987).
- [10] Babrauskas, V., Levin, B. C., and Gann, R. G., A New Approach to Fire Toxicity Data for Hazard Evaluation. **ASTM Standardization News**. 14, 28-33 (1986).
- [11] Levin, B.C., Paabo, M., Bailey, C., Harris, S.E., and Gurman, J.L., Toxicological Effects of the Interactions of Fire Gases and Their Use in a Toxic Hazard Assessment Computer Model, *The Toxicologist*, 5:127 (1985).
- [12] Levendusky, T. L. and Musselman, L. L., Precipitated Alumina Trihydrate for Polymers, presented at 1984 RETEC, Society of Plastics Engineers, Georgia Institute of Technology, Atlanta, Ga, 1984.

- [13] Babrauskas, V., Development of the Cone Calorimeter -- A Bench-Scale Heat Release Rate Apparatus Based on Oxygen Consumption (NBSIR 82-2611). [U.S.] Nat. Bur. Stand. (1982).
- [14] Babrauskas, V., The Cone Calorimeter -- A Versatile Bench-Scale Tool for the Evaluation of Fire Properties, pp. 78-87 in **New Technology to Reduce Fire Losses & Costs**, S.J. Grayson and D.A. Smith, eds., Elsevier Applied Science Publishers, London (1986).
- [15] Huggett, C., Estimation of Rate of Heat Release by Means of Oxygen Consumption Measurements. **Fire and Materials**. **4**, 61-65 (1980).
- [16] Babrauskas, V., and Mulholland, G., Smoke and Soot Data Determinations in the Cone Calorimeter, pp. 83-104 in **Mathematical Modeling of Fires** (ASTM STP 983), American Society for Testing and Materials, Philadelphia (1987).
- [17] Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products using an Oxygen Consumption Calorimeter (E 1354-90a). **Annual Book of ASTM Standards**, Vol. 04.07, American Society for Testing and Materials (1991).
- [18] Babrauskas, V., Harris, R.H., Jr., Gann, R.G., Levin, B.C., Lee, B.T., Peacock, R.D., Paabo, M., Twilley, W., Yoklavich, M.F., and Clark, H.M., Fire Hazard Comparison of Fire-Retarded and Non-Fire-Retarded Products (NBS Special Publication SP 749). [U.S.] Natl. Bur. Stand. (1988).
- [19] Levin, B. C., Paabo, M., Gurman, J. L. and Harris, S. E., Effects of Exposure to Single or Multiple Combinations of the Predominant Toxic Gases and Low Oxygen Atmospheres Produced in Fires, *Fundam. Appl. Tox.* **9**:236-250 (1987).
- [20] Levin, B. C., Paabo, M., Gurman, J. L., Harris, S. E., and Braun, E., Toxicological Interactions between Carbon Monoxide and Carbon Dioxide. *Toxicology* **47**:135-164 1987.
- [21] Babrauskas, V., Harris, Jr., R. H., Braun, E., Levin, B., Paabo, M. and Gann, R. G., The Role of Bench-Scale Test Data in Assessing Real-Scale Fire Toxicity, NIST TN 1284, National Institute of Standards and Technology, 1991.
- [22] Paabo, M. and Levin, B.C., A Literature Review of the Chemical Nature and Toxicity of the Thermal Decomposition Products of Polyethylenes. *Fire and Matls.* **11**:55-70 (1987).
- [23] Levin, B.C., A Summary of the NBS Literature Reviews on the Chemical Nature and Toxicity of the Pyrolysis and Combustion Products from Seven Plastics:Acrylonitrile-Butadiene Styrenes (ABS), Nylons, Polyesters, Polyethylenes, Polystyrenes, Poly(vinyl chlorides), and Rigid Polyurethane Foams. *Fire and Matls.* **11**:143-157 (1987).

Table 1. Materials Studied

Sample No.	Code	Polymer Type/Fillers	Additive	Additive conc. (Z by wt.)
1	CC	Isophthalic acid PES ^a /styrene/glass	CaCO ₃	55
2	QQ	Isophthalic acid PES/styrene/glass	ATH	54
3	XX	Brominated PES/styrene/glass	Br/Sb ₂ O ₃ /ATH	4/1/50
4	AA	Chlorinated PES/styrene/glass	Cl/Sb ₂ O ₃	8/1.5
23	II	Acrylic-based PES/styrene/glass	ATH	43
32	--	GP ^b unsaturated PES/glass	CaCO ₃	50
33	--	GP unsaturated PES/glass	ATH	50
34	--	GP/Br unsaturated PES/glass	Br/Sb ₂ O ₃ /ATH	2.5/0.5/48
35	--	GP/Br unsaturated PES/glass	Br/Sb ₂ O ₃ /ATH/NPS	2.5/0.5/24/24
5	VV	High Density Polyethylene	None	--
6	HH	High Density Polyethylene	CaCO ₃	60
7	BB	High Density Polyethylene	ATH	60
8	EE	High Density Polyethylene	Br/Sb ₂ O ₃	13/6
9	MM	High Density Polyethylene	Na aluminocarbonate	58
11	PP	High Density Polyethylene	Mg(OH) ₂	60
25	AC	Low Density Polyethylene	ATH	45
26	AD	Low Density Polyethylene	ATH	50
27	AE	Low Density Polyethylene	ATH	55
28	AF	XL ^c Low Density Polyethylene	ATH	50
29	AG	XL Low Density Polyethylene	ATH	55
30	AH	XL Low Density Polyethylene	Br/Sb ₂ O ₃ /ATH	11/5/10
31	AJ	XL Low Density Polyethylene	Cl/Sb ₂ O ₃ /ATH	10/5/10
12	LL	Polypropylene	None	--
13	FF	Polypropylene	CaCO ₃	58
14	GG	Polypropylene	ATH	57
15	UU	Polypropylene	Br/Sb ₂ O ₃	14/6
19	201-65,66	Flexible poly(vinyl chloride)/clay	None	--
20	201-63,64	Flexible poly(vinyl chloride)/clay	CaCO ₃	15
21	201-61,62	Flexible poly(vinyl chloride)/clay	ATH	15
16	201-67	Rigid poly(vinyl chloride)	None	--
17	AB,201-611-613	Rigid poly(vinyl chloride)	CaCO ₃	30
18	201-68,69 201-610	Rigid poly(vinyl chloride)	ATH	30
36	--	Rigid poly(vinyl chloride)	None	--
37	--	Rigid poly(vinyl chloride)	CaCO ₃	30
38	--	Rigid poly(vinyl chloride)	ATH	30
39	--	Rigid poly(vinyl chloride)	Mg(OH) ₂	30
40	--	XL Ethylene-vinyl acetate	None	--
41	--	XL Ethylene-vinyl acetate	ATH	65
42	--	XL Ethylene-vinyl acetate	Cl/Sb ₂ O ₃	15/4
43	--	XL Ethylene-vinyl acetate	Mg(OH) ₂	65
44	--	TP ^d Ethylene-vinyl acetate	None	--
45	--	TP Ethylene-vinyl acetate	ATH	65
46	--	TP Ethylene-vinyl acetate	Cl/Sb ₂ O ₃	15/4

a: Polyester

b: General purpose

c: XL = cross-linked

d: TP = Thermoplastic formulation

Table 2. Cone Calorimeter Data Summary -- 30 kW/m² Irradiance Tests without Spark Igniter^a

Sample ID	Polymer type	FR additive	mass (g)	% mass consumed	Ign. time (s)	Peak q" (kW/m ²)	Peak time (s)	Total q" (MJ/m ²)	Eff. Δh _c (MJ/kg)
1 -CC	Isob PES	CaCO ₃	120.5	24.2	333	248	335	66	22
2 -QQ	Isopes	ATH	106.0	NI	NI	NI	NI	NI	NI
3 -XX	BrPES	Br/Sb ₂ O ₃ / ATH	124.0	NI	NI	NI	NI	NI	NI
4 -AA	ClPES	Cl/Sb ₂ O ₃	113.5	NI	NI	NI	NI	NI	NI
23-II	Acr ^c PES	ATH	122.6	NI	NI	NI	NI	NI	NI
5 -VV	HDPE	None	45.0	88.4	205	1759	360	166	54
6 -HH	HDPE	CaCO ₃	76.8	37.8	286	299	516	102	60
7 -BB	HDPE	ATH	74.5	NI	NI	NI	NI	NI	NI
8 -EE	HDPE	Br/Sb ₂ O ₃	47.4	85.0	377	1279	NI	117	56
9 -MM	HDPE	Na Aluminocarbonate	63.8	48.4	376	263	385	99	32
11-PP	HDPE	Mg(OH) ₂	72.5	NI	NI	NI	NI	NI	NI
25-AC	LDPE	ATH	45.3	48.0	293	255	315	77	35
26-AD	LDPE	ATH	57.8	54.3	177	172	185	99	31
27-AE	LDPE	ATH	56.0	NI	NI	NI	NI	NI	NI
28-AF	XLPE	ATH	91.7	NI	NI	NI	NI	NI	NI
29-AG	XLPE	ATH	97.3	NI	NI	NI	NI	NI	NI
30-AH	XLPE	Br/Sb ₂ O ₃ / ATH	84.3	57.4	522	162	545	77	16
31-AJ	XLPE	Cl/Sb ₂ O ₃ / ATH	74.2	NI	NI	NI	NI	NI	NI

Table 2 (cont). Cone Calorimeter Data Summary -- 30 kW/m² Irradiance Tests without Spark Igniter^a

Sample ID	Polymer type	FR additive	mass (g)	% mass consumed	Ign. time (s)	Peak q" (kW/m ²)	Peak time (s)	Total q" (MJ/m ²)	Eff. Δh _c (MJ/kg)
12-LL	PP	None	36.5	85.6	209	1600	285	110	59
13-FF	PP	CaCO ₃	61.1	32.5	- ^d	25	380	9	7
14-GG	PP	ATH	57.8	NI	NI	NI	NI	NI	NI
15-UU	PP	Br/Sb ₂ O ₃	52.7	66.2	272	456	355	62	18

a: No sample replication in this table

b: Isophthalic acid resin

c: Acrylic-based resin

d: Not obtained, operator error

NI: No Ignition

Table 3. Cone Calorimeter Data Summary -- Test Average Data
at 30 kW/m² Irradiance without Spark Igniter^a

Sample ID	Polymer type	FR additive	CO (kg/kg)	CO ₂ (kg/kg)	Smoke (m ² /kg)
1 -CC	Iso ^b PES	CaCO ₃	0.041	1.782	523
2 -QQ	IsoPES	ATH	NI	NI	NI
3 -XX	BrPES	Br/Sb ₂ O ₃ /ATH	NI	NI	NI
4 -AA	ClPES	Cl/Sb ₂ O ₃	NI	NI	NI
23-II	Acr ^c PES	ATH	NI	NI	NI
5 -VV	HDPE	None	0.027	2.845	513
6 -HH	HDPE	CaCO ₃	0.034	2.245	1087
7 -BB	HDPE	ATH	NI	NI	NI
8 -EE	HDPE	Br/Sb ₂ O ₃	0.012	1.853	702
9 -MM	HDPE	Na Alumino- carbonate	0.014	2.061	212
11-PP	HDPE	Mg(OH) ₂	NI	NI	NI
25-AC	LDPE	ATH	0.021	2.096	347
26-AD	LDPE	ATH	0.022	1.888	99
27-AE	LDPE	ATH	NI	NI	NI
28-AF	XLPE	ATH	NI	NI	NI
29-AG	XLPE	ATH	NI	NI	NI
30-AH	XLPE	Br/Sb ₂ O ₃ /ATH	0.155	0.644	1366
31-AJ	XLPE	Cl/Sb ₂ O ₃ /ATH	NI	NI	NI
12-LL	PP	None	0.033	2.312	749
13-FF	PP	CaCO ₃	0.029	0.196	607
14-GG	PP	ATH	NI	NI	NI
15-UU	PP	Br/Sb ₂ O ₃	0.151	0.696	1258

a: No sample replication in this table

b: Isophthalic acid resin

c: Arylic-based resin

NI No ignition

Table 4. Cone Calorimeter Data Summary -- 30 kW/m² Irradiance Tests with Spark Igniter

Sample ID	Polymer type	FR additive	Mass (g)	% mass consumed	Ign. time (s)	Peak q (kW/m ²)	Peak time (s)	Total q" (MJ/m ²)	Eff. Δh _c (MJ/kg)
1 -CC ^a	Iso ^d PES	CaCO ₃	118	28.5	206	261	223	72	22
2 -QQ ^b	IsoPES	ATH	109	39.4	256	143	295	77	18
3 -XX ^c	BrPES	Br/Sb ₂ O ₃ / ATH	122	34.1	360	73	403	52	12
4 -AA ^c	ClPES	Cl/Sb ₂ O ₃	111	42.9	238	76	618	24	5
23-II ^b	Acr ^e PES	ATH	119	40.7	318	128	953	69	14
32 ^a	PES	CaCO ₃	70	25.6	160	186	240	44	24
33 ^a	PES	ATH	73	35.8	295	110	572	48	18
34 ^a	Br/PES	ATH	75	33.2	320	95	612	45	18
35 ^a	Br/PES	ATH/NPS	74	28.8	248	118	465	41	19
5 -VV ^b	HDPE	None	45	87.7	168	1803	350	172	59
6 -HH ^b	HDPE	CaCO ₃	78	37.5	224	280	475	113	60
7 -BB ^b	HDPE	ATH	74	51.0	178	114	250	99	43
8 -EE ^a	HDPE	Br/Sb ₂ O ₃	48	90.7	153	1015	295	82	58
9 -MM ^b	HDPE	Na Alumino- carbonate	65	56.8	218	176	275	113	31
11-PP ^b	HDPE	Mg(OH) ₂	74	56.0	330	132	1085	118	53
25-AC ^b	LDPE	ATH	48	63.3	141	245	210	101	33
26-AD ^b	LDPE	ATH	54	58.5	126	207	190	96	31
27-AE ^b	LDPE	ATH	62	61.0	111	196	170	117	31
28-AF ^b	XLPE	ATH	92	61.3	388	245	1160	154	28
29-AG ^b	XLPE	ATH	98	54.6	321	151	1230	142	27
30-AH ^c	XLPE	Br/Sb ₂ O ₃ / ATH	87	69.6	313	157	505	96	16
31-AJ ^b	XLPE	Cl/Sb ₂ O ₃ / ATH	75	54.7	314	219	350	103	25

Table 4 (cont). Cone Calorimeter Data Summary -- 30 kW/m² Irradiance Tests with Spark Igniter

Sample ID	Polymer type	FR additive	Mass (g)	% mass consumed	Ign. time (s)	Peak q (kW/m ²)	Peak time (s)	Total q" (MJ/m ²)	Eff. Δh _c (MJ/kg)
12-LL ^b	PP	None	36	86.1	83	1555	225	130	60
13-FF ^b	PP	CaCO ₃	61	36.6	104	312	315	88	59
14-GG ^b	PP	ATH	58	56.7	154	174	225	93	45
15-UU ^b	PP	Br/Sb ₂ O ₃	57	92.6	151	400	335	95	18
19 ^c	F-PVC	None	26	88.6	29	286	63	33	14
20 ^c	F-PVC	CaCO ₃	29	75.7	35	205	63	32	14
21 ^c	F-PVC	ATH	28	78.1	33	161	73	31	14
16 ^b	R-PVC	None	57	44.9	156	98	180	7	3
17 ^c	R-PVC	CaCO ₃	56	31.6	114	141	138	7	4
18 ^b	R-PVC	ATH	58	34.2	224	42	260	2	1
36 ^a	R-PVC	None	50	54.1	238	118	298	29	11
37 ^c	R-PVC	CaCO ₃	58	46.1	158	61	635	31	12
38 ^c	R-PVC	ATH	58	18.0	707	56	843	18	11
39 ^c	R-PVC	Mg(OH) ₂	57	22.2	406	59	573	18	13
40 ^a	XL-EVA	None	32	68.2	147	463	283	67	31
41 ^a	XL-EVA	ATH	55	47.8	268	110	740	62	24
42 ^a	XL-EVA	Cl/Sb ₂ O ₃	49	48.0	155	107	273	39	17
43 ^a	XL-EVA	Mg(OH) ₂	53	44.0	248	167	375	53	23
44 ^a	TP-EVA	None	43	63.7	90	574	238	55	27
45 ^a	TP-EVA	ATH	54	49.5	141	83	220	55	21
46 ^a	TP-EVA	Cl/Sb ₂ O ₃	49	61.0	112	170	133	57	19

a: Average of three values

b: Single value only

c: Average of two values

d: Isophthalic acid resin

e: Acrylic-based resin

NI No ignition

Table 5. Cone Calorimeter Data Summary -- Test Average Data at 30 kW/m²
Irradiance with Spark Igniter

Sample ID	Polymer type	FR additive	CO (kg/kg)	CO ₂ (kg/kg)	HCl (kg/kg)	HBr (kg/kg)	Smoke (m ² /kg)
1 -CC ^a	Iso ^d PES	CaCO ₃	0.039	1.723	NA	NA	519
2 -QQ ^b	IsoPES	ATH	0.034	1.336	NA	NA	118
3 -XX ^c	BrPES	Br/Sb ₂ O ₃ /ATH	0.089	0.806	ND	0.020	433
4 -AA ^c	ClPES	Cl/Sb ₂ O ₃	0.072	0.350	0.1	ND	507
23-II ^b	Acr ^e PES	ATH	0.009	1.240	NA	NA	129
32 ^a	PES	CaCO ₃	0.050	1.918	NA	NA	1035
33 ^a	PES	ATH	0.044	1.517	NA	NA	495
34 ^a	Br/PES	ATH	0.057	1.406	NA	NA	468
35 ^a	Br/PES	ATH/NPS	0.068	1.468	NA	NA	847
5 -VV ^b	HDPE	None	0.025	2.914	NA	NA	474
6 -HH ^b	HDPE	CaCO ₃	0.026	2.483	NA	NA	876
7 -BB ^b	HDPE	ATH	0.043	1.725	NA	NA	61
8 -EE ^a	HDPE	Br/Sb ₂ O ₃	0.080	0.907	ND	0.056	1265
9 -MM ^b	HDPE	Na Alumino- carbonate	0.012	1.987	NA	NA	189
11-PP ^b	HDPE	Mg(OH) ₂	0.017	1.912	NA	NA	230
25-AC ^b	LDPE	ATH	0.014	2.005	NA	NA	282
26-AD ^b	LDPE	ATH	0.017	1.940	NA	NA	117
27-AE ^b	LDPE	ATH	0.022	1.833	NA	NA	221
28-AF ^b	XLPE	ATH	0.018	1.672	NA	NA	356
29-AG ^b	XLPE	ATH	0.011	1.577	NA	NA	201
30-AH ^c	XLPE	Br/Sb ₂ O ₃ /ATH	0.152	0.647	ND	0.081	1445
31-AJ ^b	XLPE	Cl/Sb ₂ O ₃ /ATH	0.082	1.307	0.077	0.007	982

Table 5 (cont). Cone Calorimeter Data Summary -- Test Average Data at 30 kW/m² Irradiance with Spark Igniter

Sample ID	Polymer type	FR additive	CO (kg/kg)	CO ₂ (kg/kg)	HCl (kg/kg)	HBr (kg/kg)	Smoke (m ² /kg)
12-LL ^b	PP	None	0.032	2.737	NA	NA	691
13-FF ^b	PP	CaCO ₃	0.031	2.482	NA	NA	1152
14-GG ^b	PP	ATH	0.019	1.879	NA	NA	288
15-UU ^b	PP	Br/Sb ₂ O ₃	0.146	0.728	ND	0.066	1258
19 ^c	F-PVC	None	0.112	0.779	0.22	ND	1032
20 ^c	F-PVC	CaCO ₃	0.071	0.750	0.15	ND	912
21 ^c	F-PVC	ATH	0.084	0.770	0.18	ND	685
16 ^b	R-PVC	None	0.018	0.124	0.61	ND	577
17 ^c	R-PVC	CaCO ₃	0.024	0.220	0.46	ND	536
18 ^b	R-PVC	ATH	0.007	0.083	0.55	ND	263
36 ^a	R-PVC	None	0.064	0.635	NA	NA	626
37 ^c	R-PVC	CaCO ₃	0.047	0.949	NA	NA	444
38 ^c	R-PVC	ATH	0.117	1.038	NA	NA	667
39 ^c	R-PVC	Mg(OH) ₂	0.071	0.869	NA	NA	691
40 ^a	XL-EVA	None	0.026	2.279	NA	NA	402
41 ^a	XL-EVA	ATH	0.026	1.625	NA	NA	269
42 ^a	XL-EVA	Cl/Sb ₂ O ₃	0.115	0.976	NA	NA	920
43 ^a	XL-EVA	Mg(OH) ₂	0.023	1.614	NA	NA	214
44 ^a	TP-EVA	None	0.019	1.965	NA	NA	330
45 ^a	TP-EVA	ATH	0.041	1.477	NA	NA	85
46 ^a	TP-EVA	Cl/Sb ₂ O ₃	0.117	1.082	NA	NA	824

a: Average of three values
 b: Single value only
 c: Average of two values
 d: Isophthalic acid resin
 e: Acrylic-based resin
 NI: No ignition
 NA: Not analyzed
 ND: Not detected

Table 6. Cone Calorimeter Data Summary -- 100 kW/m² Irradiance Tests
without Spark Igniter^a

Sample ID	Polymer type	FR additive	mass (g)	% mass consumed	Ign. time (s)	Peak q" (kW/m ²)	Peak time (s)	Total q" (MJ/m ²)	Eff. Δh _c (MJ/kg)
5 -VV	HDPE	None	46.8	83.6	24	2643	120	171	48.6
7 -BB	HDPE	ATH	75.2	56.7	25	310	410	120	50.5
8 -EE	HDPE	Br/Sb ₂ O ₃	50.9	84.3	24	1756	105	94	47.4

a: No sample replication in this table

Table 7. Cone Calorimeter Data Summary -- Test Average Data at 100 kW/m² Irradiance without Spark Igniter^a

<u>Sample ID</u>	<u>Polymer type</u>	<u>FR additive</u>	<u>CO (kg/kg)</u>	<u>CO₂ (kg/kg)</u>	<u>Smoke (m²/kg)</u>
5 -VV	HDPE	None	0.029	3.345	315
7 -BB	HDPE	ATH	0.017	1.802	521
8 -EE	HDPE	Br/Sb ₂ O ₃	0.031	1.075	722

a: No sample replication in this table

Table 8. Chemical and Toxicological Results from Material 5-VV

Mode	Expt. Temp. (°C)	Animals Exposed	Mass Loaded		Gas Concentration ^a		No. Deaths/No. Tested		Latest Day of Death	Predict ^b Deaths
			(g/m ³)	Consumed	CO (ppm)	CO ₂ (ppm)	Within Exposure	Within Plus Post		
F	400	No	40	40	1470	34100	-	-	-	No
	398	Yes	40	40	1640	38600	0/6	0/6 ^c	-	No
	399	Yes	39	39	1440	35500	0/6	1/6	1	No
NF	349	No	39	17	1270	300	-	-	-	No
	349	Yes	40	9	250	3050	0/6	0/6	-	No
	349	Yes	40	1	90	3400	0/6	0/6	-	No
	377	Yes	20	17	2330	3190	0/6	6/6	1	No
	374	Yes	30	21	2020	4430	0/6	6/6	1	No
	373	Yes	39	29	3620	3420	2/6	6/6	0	No

a: Average concentration over 30 minute exposure

b: Prediction of deaths based on concentrations of CO and CO₂ and knowledge of their toxicological interactions.

c: One animal lost 140 grams of weight and was very sick when sacrificed on day 39 following the exposure.

F: Flaming

NF: Non-Flaming

Table 9. Chemical and Toxicological Results from Material 6-HH

Mode	Expt. Temp. (°C)	Animals Exposed	Mass Loaded (g/m ³)	Gas Concentration ^a		No. Deaths/No. Tested		Latest Day of Death	Predict ^b Deaths
				CO (ppm)	CO ₂ (ppm)	Within Exposure	Within Plus Post		
F	474	No	28	540	15000	-	-	-	No
	475	No	40	710	22200	-	-	-	No
NF	476	Yes	30	550	19300	0/6	0/6	-	No
	473	Yes	40	670	22600	0/6	0/6	-	No
NF	426	No	25	850	1960	-	-	-	No
	424	No	40	1300	2590	-	-	-	No
NF	425	Yes	30	1100	4450	0/6	5/6	3	No
	424	Yes	40	1500	4740	0/6	6/6	2	No

a: Average concentration over 30 minute exposure

b: Prediction of deaths based on concentrations of CO and CO₂ and knowledge of their toxicological interaction.

F: Flaming

NF: Non-Flaming

Table 10. Chemical and Toxicological Results from Material 7-BB

Mode	Expt. Temp. (°C)	Animals Exposed	Mass		Gas Concentration ^a		No. Deaths/No. Tested		Latest Day of Death	Predict ^b Deaths
			Loaded	Consumed (g/m ³)	CO (ppm)	CO ₂ (ppm)	Within Exposure	Within Plus Post		
F	575	No	20	12	380	13000	-	-	-	No
		No	30	18	610	17500	-	-	-	No
		No	40	24	830	23000	-	-	-	No
	Yes	40	24	730	25600	0/6	0/6	-	No	
NF	425	Yes	30	15	940	2800	0/6	2/6	2	No
		Yes	35	19	1200	3400	0/6	2/6	2	No
	Yes	40	24	1700	3800	0/6	6/6	1	No	
	Yes	40	23	1400	9900	1/6	2/6	5	No	

a: Average concentration over 30 minute exposure

b: Prediction of deaths based on concentrations of CO and CO₂ and knowledge of their toxicological interaction.

F: Flaming

NF: Non-Flaming

NF-F: Material flamed - 10 minutes into the test.

Table 11. Chemical and Toxicological Results from Material 8-EE

Mode	Expt. Temp. (°C)	Animals Exposed	Mass Loaded Consumed		Gas Concentration ^a		No. Deaths/No. Tested		Latest Day of Death	Predict ^b Deaths
			(g/m ³)	(g/m ³)	CO (ppm)	CO ₂ (ppm)	Within Exposure	Within Plus Post		
F ^c	425	No	20	19	1600	11200	-	-	-	No
		No	25	25	2400	13700	-	-	-	No
		No	40	40	3800	13200	-	-	-	Yes
		Yes	39	39	3700	17700	0/6	2/6	3	Yes
		Yes	40	39	3700	12900	1/6	4/6	4	Yes
NF	375	No	20	16	160	280	-	-	-	No
		No	40	33	320	480	-	-	-	No
		Yes	40	34	560	2100	0/6	0/6	-	No
		Yes	40	33	490	2100	0/6	0/6	-	No

a: Average concentration over 30 minute exposure

b: Prediction of deaths based on concentrations of CO and CO₂ and knowledge of their toxicological interactions.

c: Flaming was not steady

F: Flaming

NF: Non-Flaming

Table 12. Chemical and Toxicological Results from Material 11-PP

Mode	Expt. Temp. (°C)	Animals Exposed	Mass		Gas Concentration ^a		No. Deaths/No. Tested		Latest Day of Death	Predict ^b Deaths
			Loaded	Consumed (g/m ³)	CO (ppm)	CO ₂ (ppm)	Within Exposure	Within Plus Post		
F	575	No	20	12	150	14200	-	-	-	No
		No	31	19	600	18300	-	-	-	No
		No	40	25	560	23800	-	-	-	No
		Yes	40	24	480	25500	0/6	0/6	-	No
		Yes	40	25	580	24800	0/6	0/6	-	No
NF	525	No	31	19	1400	3300	-	-	-	No
	500	No	32	19	1700	3700	-	-	-	No
		No	37	22	2000	4600	-	-	-	No
		Yes	20	12	1000	4900	0/6	5/6	1	No
		Yes	22	13	1100	4700	0/6	1/6	1	No
		Yes	25	15	1300	5300	0/6	4/6	24	No
		Yes	30	18	1400	5300	0/6	6/6	2	No
		Yes	35	21	1800	6700	0/6	6/6	3	No
		Yes	40	24	2000	6500	0/6	6/6	3	No
		Yes	40	24	2100	6400	0/6	6/6	2	No

a: Average concentration over 30 minute exposure

b: Prediction of deaths based on concentrations of CO and CO₂ and knowledge of their toxicological interactions.

F: Flaming

NF: Non-Flaming

Table 13. Summary of Chemical and Toxicological Results - Non-flaming

Code	Material	Additive	Expt. Temp. (°C)	Mass Loaded Consumed (g/m ³)		% Loss	Gas Concentration (ppm)		Deaths Within Exp.	Within & Post	Latest Day of Death
				CO	CO ₂		CO	CO ₂			
5-VV	HDPE	none	350	40	9	23	250	3050	0/6	0/6	-
				40	1	3	90	3400	0/6	0/6	-
6-HH	HDPE	CaCO ₃	375	20	17	85	2330	3190	0/6	6/6	1
				30	21	70	2020	4430	0/6	6/6	1
				39	29	74	3620	3420	2/6	6/6	0
7-BB	HDPE	ATH	425	30	12	40	1100	4450	0/6	5/6	3
				35	19	54	1500	4740	0/6	6/6	2
8-EE	HDPE	Br/Sb ₂ O ₃	375	40	15	50	940	2800	0/6	2/6	2
				40	33	54	1200	3400	0/6	2/6	2
11-PP	HDPE	Mg(OH) ₂	500	40	24	60	1700	3800	0/6	6/6	1
				40	34	85	560	2100	0/6	0/6	-
				40	33	83	490	2100	0/6	0/6	-
				20	12	60	1000	4900	0/6	5/6	1
				22	13	59	1100	4700	0/6	1/6	1
				25	15	60	1300	5300	0/6	4/6	24
30	18	60	1400	5300	0/6	6/6	2				
35	21	60	1800	6700	0/6	6/6	6/6	3			
40	24	60	2000	6500	0/6	6/6	6/6	3			
40	24	60	2100	6400	0/6	6/6	6/6	2			

Table 14. Summary of Chemical and Toxicological Results - Flaming

Code	Material	Additive	Expt. Temp. (°C)	Mass Loaded		% Loss	Gas Concentration (ppm)		Deaths Within Exp.	Within & Post	Latest Day of Death
				(g/m ³)	Consumed		CO	CO ₂			
5-VV	HDPE	none	400	40	40	100	1640	38600	0/6	0/6*	-
				39	39	100	1440	35500	0/6	1/6	1
6-HH	HDPE	CaCO ₃	475	30	13	43	550	19300	0/6	0/6	-
				40	16	40	670	22600	0/6	0/6	-
7-BB	HDPE	ATH	575	40	24	60	730	25600	0/6	0/6	-
				40	24	60	-	-	0/6	0/6	-
8-EE	HDPE	Br/Sb ₂ O ₃	425	39	39	98	3700	17700	0/6	2/6	3
				40	39	98	3700	12900	1/6	4/6	4
11-PP	HDPE	Mg(OH) ₂	575	40	24	60	480	25500	0/6	0/6	-
				40	25	63	580	24800	0/6	0/6	-

* One animal lost 140 grams of weight and was very sick when sacrificed on day 39 following the experiment.

Table 15. Estimated Toxic Potency from High Density Polyethylene with and without Fire Retardants

<u>Material</u>	<u>Additive</u>	<u>ID</u>	<u>LC₅₀ Values *</u>			
			<u>WE</u>	<u>WE & PE</u>	<u>consumed (g/m³)</u>	<u>WE & PE</u>
Flaming Mode						
HDPE	none	5-VV	>40	>40	>40	>40
	CaCO ₃	6-HH	>40	>40	>16	>16
	ATH	7-BB	>40	>40	>24	>24
	Br/Sb ₂ O ₃	8-EE	>40	~39.5	>39	39
	Mg(OH) ₂	11-PP	>40	>40	>25	>25
Non-flaming Mode						
HDPE	none	5-VV	>39	<20	>29	<17
	CaCO ₃	6-HH	>40	<30	>16	<12
	ATH	7-BB	>40	35-40	>24	19-24
	Br/Sb ₂ O ₃	8-EE	>40	>40	>34	>34
	Mg(OH) ₂	11-PP	>40	20-25	>24	12-15

WE - Within exposure

PE - Post exposure

* Mass (loaded into furnace or consumed) of material divided by exposure chamber volume (g/m³) which causes 50% of the rats to die during the 30 min exposure (WE) or during the 30 minute exposure plus 14 day post-exposure period (WE & PE)

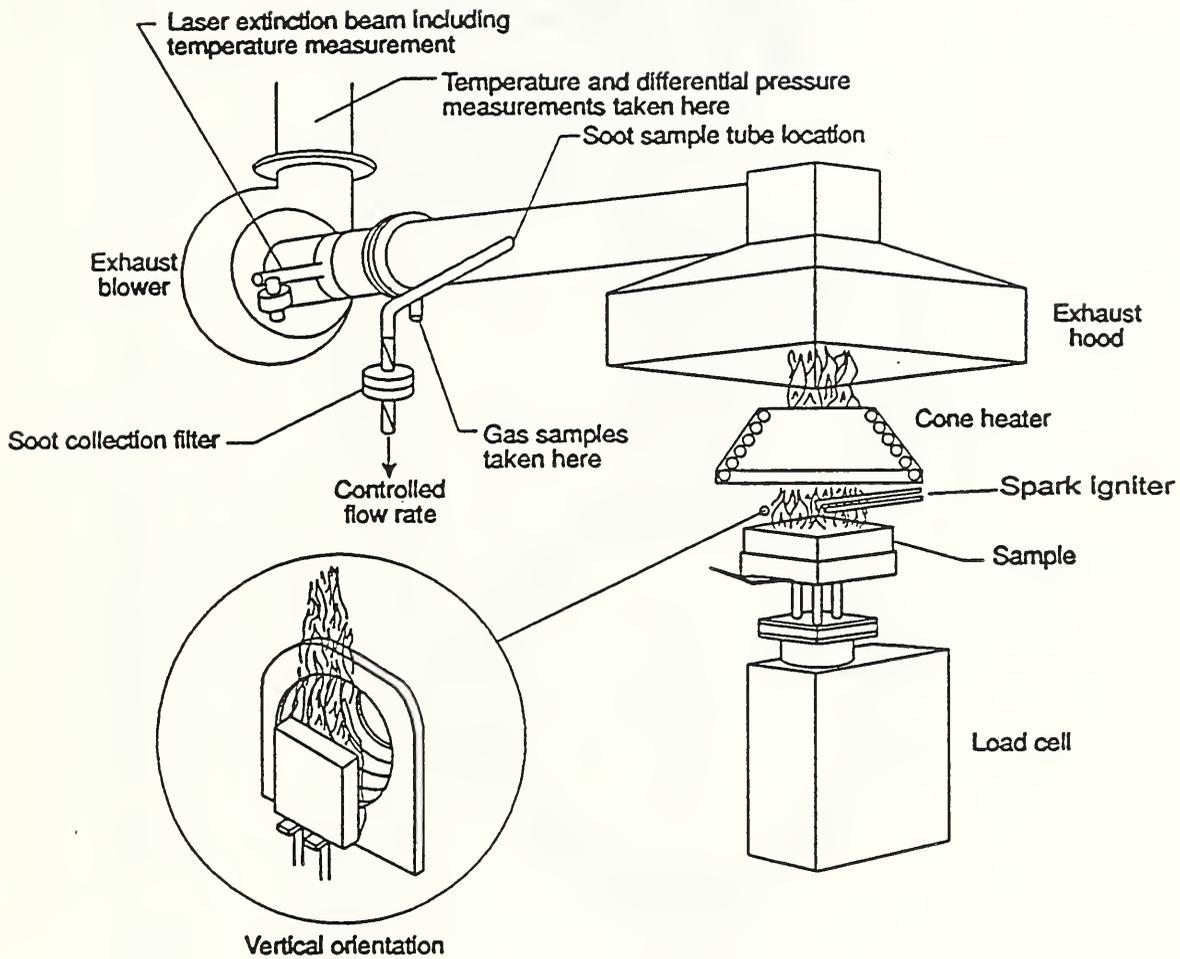


Figure 1. Conceptual View of the Cone Calorimeter

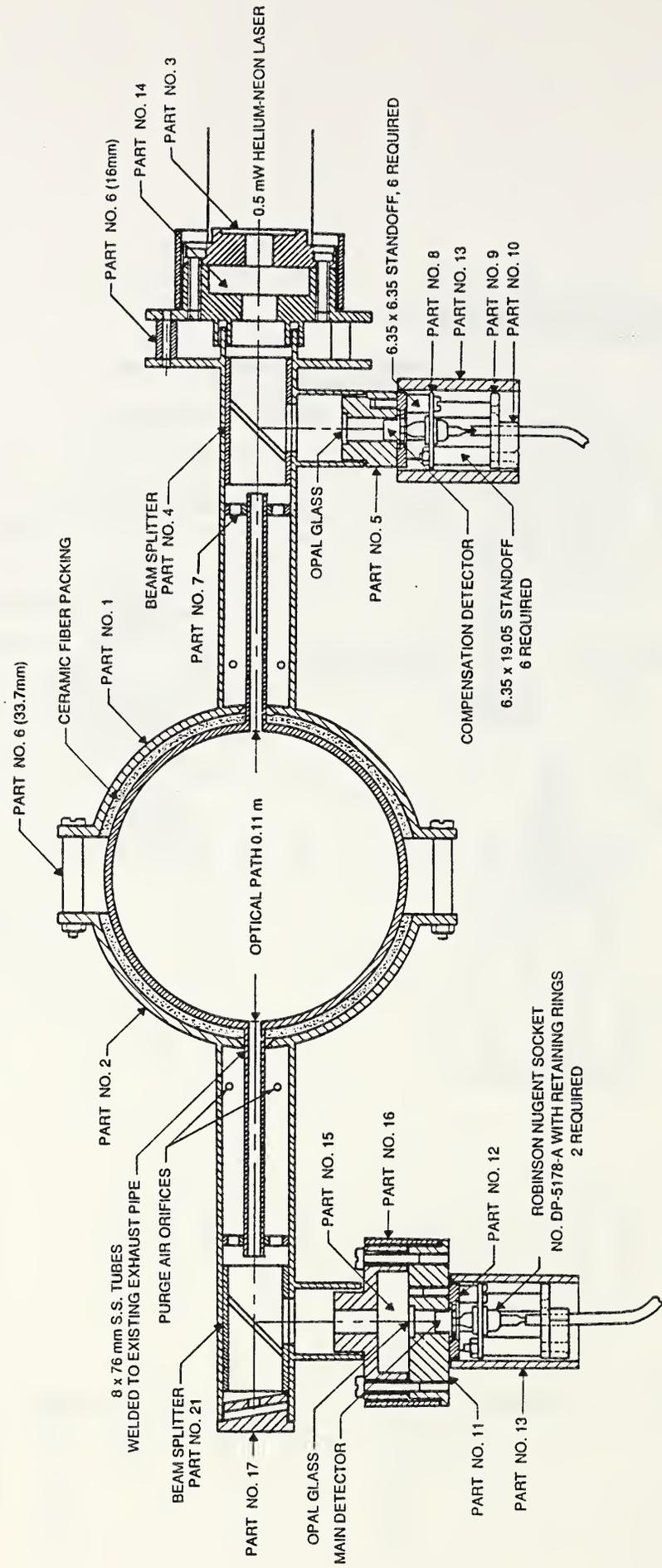


Figure 2. Smoke measurement system used on the Cone Calorimeter

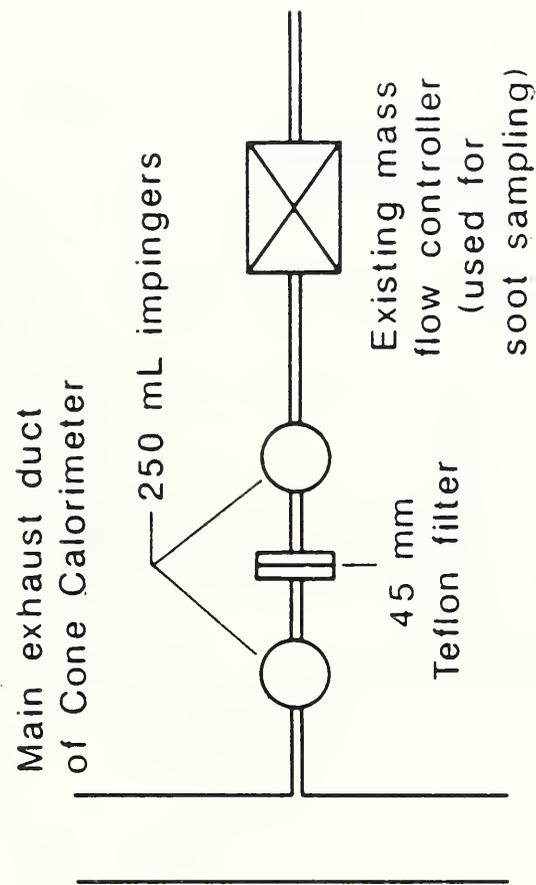


Figure 3. Impinger gas sampling in the Cone Calorimeter

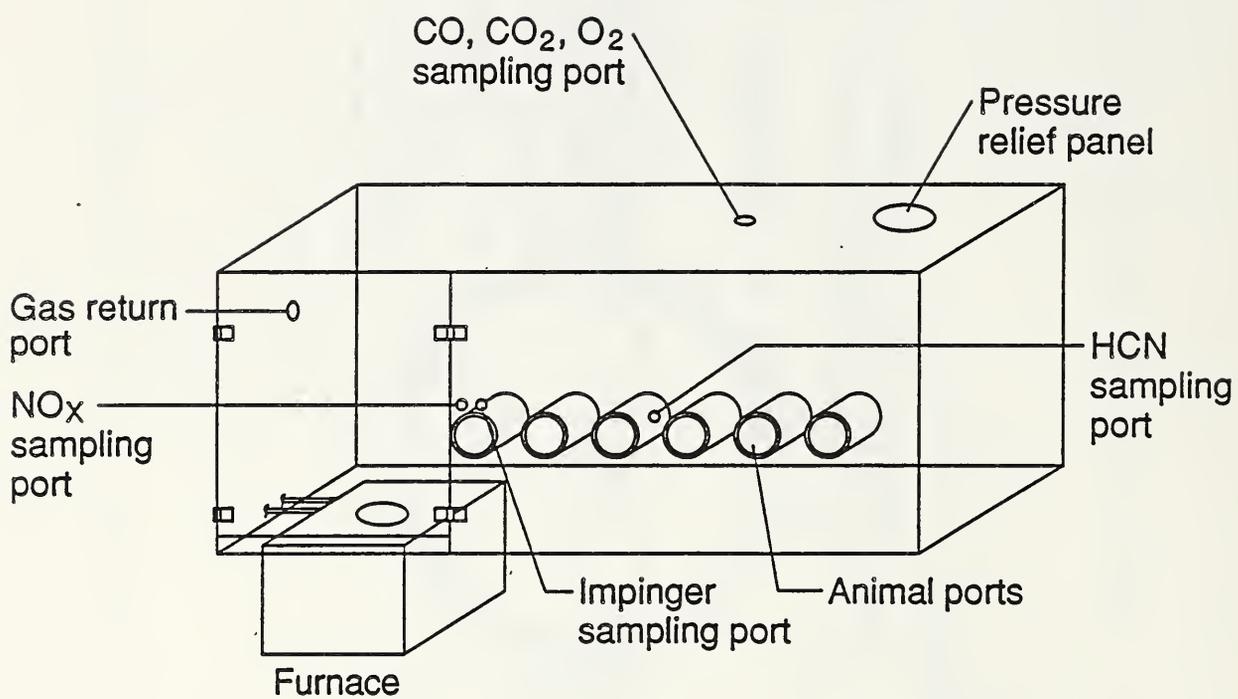


Figure 4. Animal Exposure System

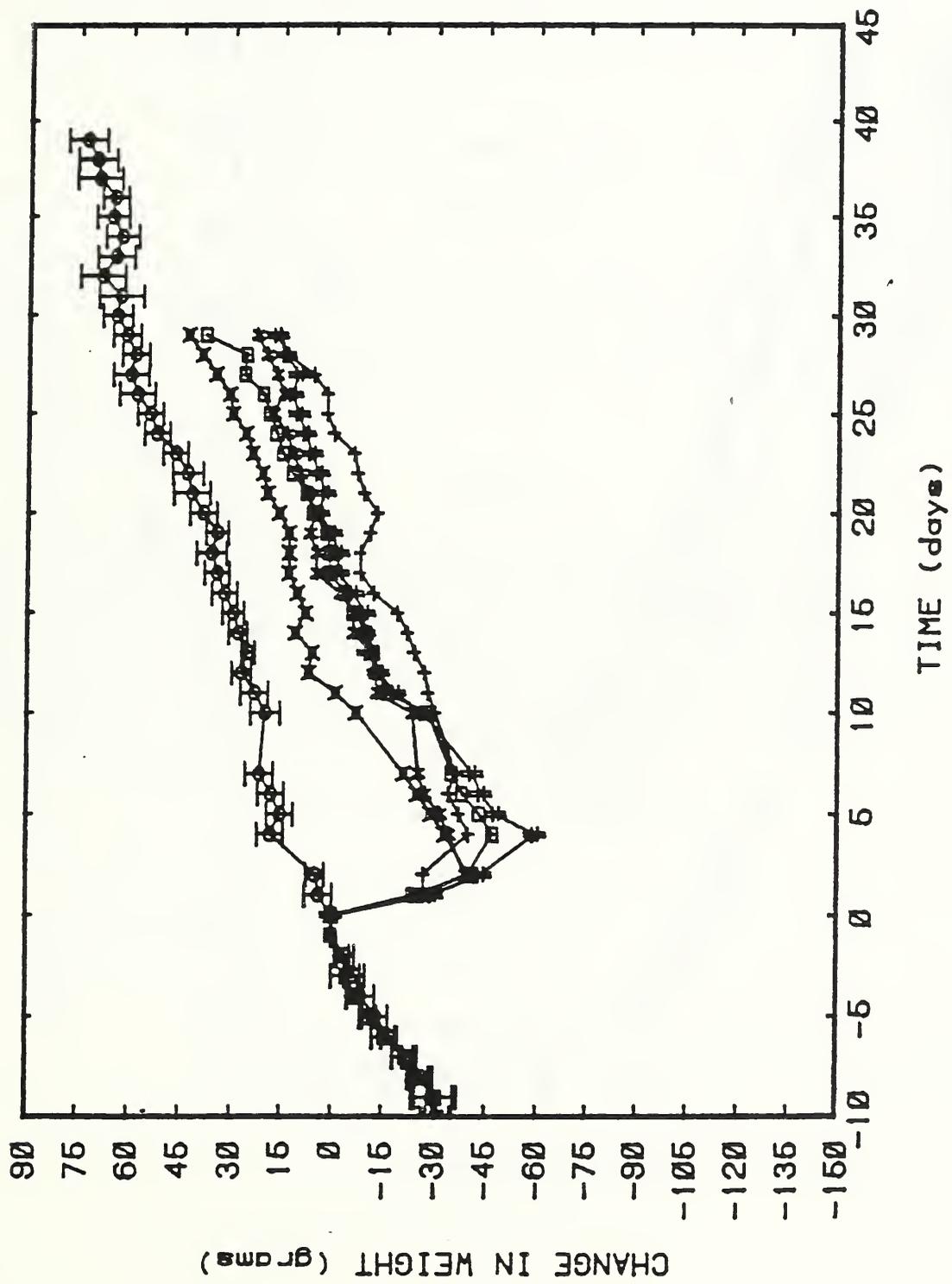


Figure 5. Post-exposure animal weight change, material 5-VV
30 min flaming exposure 39 g/m mass loading

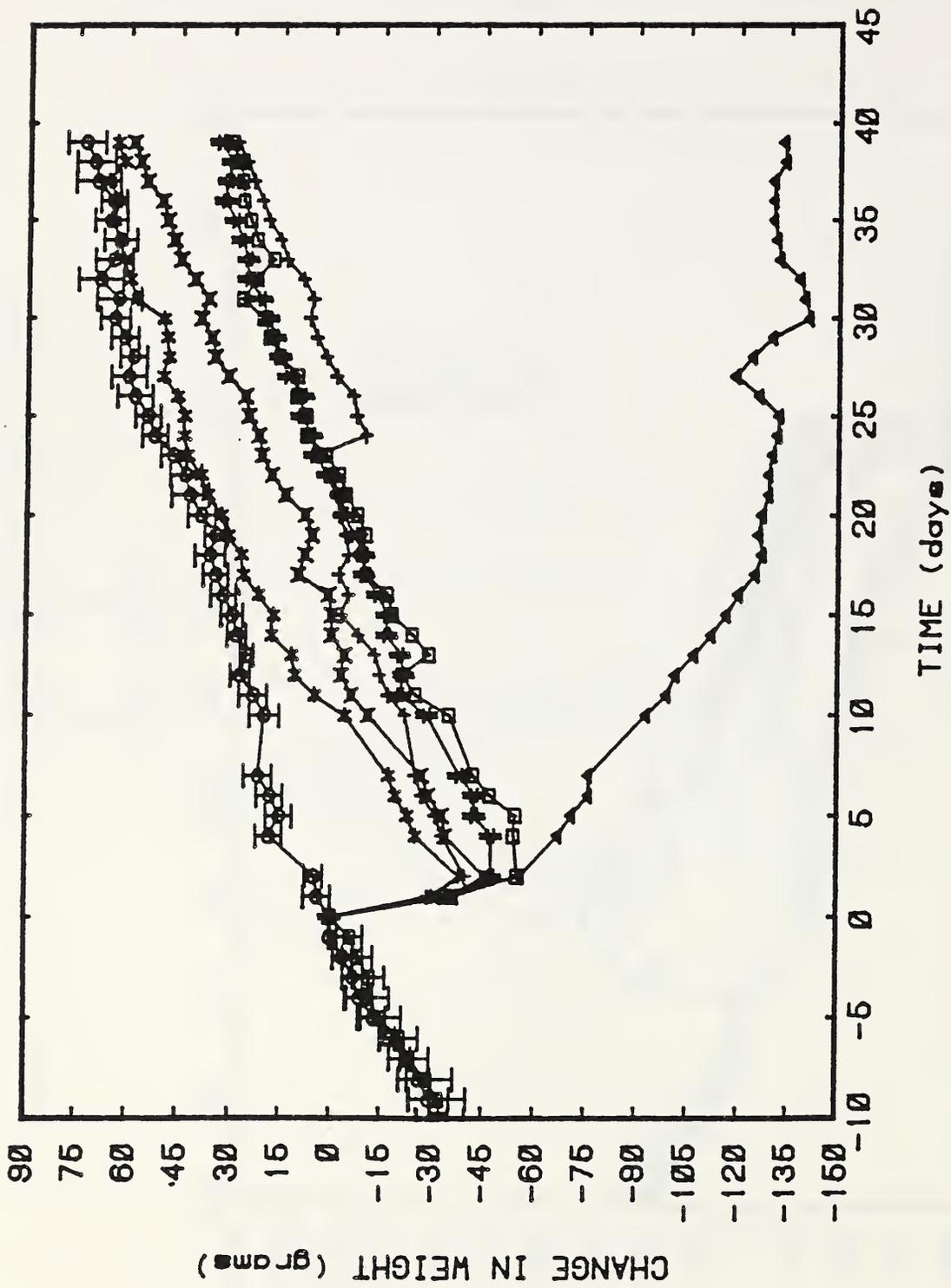


Figure 6. Post-exposure animal weight change, material 5-VV
30 min flaming exposure, 40 g/m mass loading

APPENDIX A. ION CHROMATOGRAPHY PROCEDURE

Apparatus

A commercially available ion chromatograph (Waters Model ILC-1 Ion/Liquid Chromatograph) equipped with a Waters 430 Total Conductivity Detector was used to analyze for Br⁻ and Cl⁻. An anion column (ICPAK-A or ICPAK-A HR) preceded by an Anion Guard-Pak Precolumn Module, all commercially available from Waters, was used. Chromatograms were recorded on a Spectra-Physics Model SP 4270 Integrator.

Reagents

All chemicals used in this work were of reagent grade quality. The water used was conditioned to 18.3 M Ω -cm and passed through a 0.45 μ m nominal porosity filter. Initially, the eluent for the ion chromatograph was 5 mM KOH; later in the study, the eluent was modified to 95% 5 mM KOH/5% acetonitrile. Stock solutions of Br⁻ and Cl⁻, nominally 1000 ppm, were prepared by dissolving 0.1489 g of KBr and 0.2100 g of KCl, respectively, in 100 mL of the eluents described above. Calibration solutions of 1.0 to 5.0 ppm for Br⁻ and Cl⁻ were prepared by serial dilution of the stock solutions with the eluents.

Chromatographic Procedure

The eluent flow rate was 1.0 mL/min. The sample loop had a volume of 100 μ L. Unknowns were diluted 1:10 with eluent. Samples and standards were loaded into the loop using a syringe and a 0.45 μ m syringe filter. The sample loop was rinsed with ca. 1 mL of the analyte solution before the sample was injected onto the column.

NIST-114A
(REV. 3-89)

U.S. DEPARTMENT OF COMMERCE
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY

BIBLIOGRAPHIC DATA SHEET

1. PUBLICATION OR REPORT NUMBER
NISTIR 4649

2. PERFORMING ORGANIZATION REPORT NUMBER

3. PUBLICATION DATE
October 1991

4. TITLE AND SUBTITLE

Data for Fire Hazard Assessment of Selected Non-halogenated and Halogenated Fire Retardants; Report of Test FR 3983

5. AUTHOR(S)

Richard H. Harris, Jr., Vytenis Babrauskas, Barbara C. Levin, Maya Paabo

6. PERFORMING ORGANIZATION (IF JOINT OR OTHER THAN NIST, SEE INSTRUCTIONS)

U.S. DEPARTMENT OF COMMERCE
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
GAITHERSBURG, MD 20899

7. CONTRACT/GRANT NUMBER

8. TYPE OF REPORT AND PERIOD COVERED

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (STREET, CITY, STATE, ZIP)

J.M. Huber Corporation/Solem Division
4940 Peachtree Industrial Blvd.
Norcross, Georgia 30071

Aluminum Company of America
Route 780, 7th Street road
Alcoa Center, Pennsylvania 15069

10. SUPPLEMENTARY NOTES

DOCUMENT DESCRIBES A COMPUTER PROGRAM; SF-185, FIPS SOFTWARE SUMMARY, IS ATTACHED.

11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

Five plastic materials, with and without fire retardants, were studied to compare the fire hazards of non-halogenated fire retardant additives with halogenated flame retardants. The plastic materials were identified by the sponsors as unsaturated polyesters, thermoplastic high density, low density and cross-linked low density polyethylenes, polypropylene, flexible and rigid poly(vinyl chlorides), and cross-linked and thermoplastic ethylene-vinyl acetate copolymers. The non-halogenated fire retardants tested were aluminum hydroxide (Al(OH)₃), also known as alumina trihydrate (ATH), sodium alumino-carbonate, and magnesium hydroxide. The halogenated flame retardants were chlorine or bromine/antimony oxides. The plastics were studied using the Cone Calorimeter and the cup furnace smoke toxicity method (high density polyethylene only). The Cone Calorimeter provided data on mass consumed, time to ignition, peak rate and peak time of heat release, total heat released, effective heat of combustion, average yields of CO, CO₂, HCl, and HBr, and average smoke obscuration. The concentrations of toxic gases generated in the cup furnace smoke toxicity method were used to predict the toxic potency of the mixed thermal decomposition products. The data from the Cone Calorimeter indicate that the non-halogenated fire retardants were, in most of the tested plastic formulations, more effective than the halogenated flame retardants in increasing the time to ignition. The non-halogenated fire retardants were also more effective in reducing the mass consumed, peak rate of heat release, total heat released, and effective heat of combustion, and in reducing the amount of smoke produced. The use of halogenated flame retardants increased smoke production and CO yields and, additionally, produced the known acid gases and toxic irritants, HCl and HBr, in measurable quantities. The chemical analytical data for the high density polyethylene samples decomposed via the cup furnace smoke toxicity method in the non-flaming mode indicated that the levels of CO and CO₂ were insufficient to cause death of the test animals (rats), but deaths did occur with all samples except the one containing the halogenated flame retardant. In the flaming mode deaths occurred during exposure to the combustion products from the non-fire retarded control and from the halogenated sample; only in the latter case were the CO and CO₂ concentrations high enough to cause the within exposure deaths. These toxicity results are unusual, but do not indicate a need for concern, since the LC₅₀ values are in the range typical of many common materials.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

Cone calorimeters; flame retardant treatments; halogenated compounds; plastics; polyethylenes; polypropylene; polyvinyl chloride; toxic hazards; toxicity.

13. AVAILABILITY

- UNLIMITED
 FOR OFFICIAL DISTRIBUTION. DO NOT RELEASE TO NATIONAL TECHNICAL INFORMATION SERVICE (NTIS).
 ORDER FROM SUPERINTENDENT OF DOCUMENTS, U.S. GOVERNMENT PRINTING OFFICE, WASHINGTON, DC 20402.
 ORDER FROM NATIONAL TECHNICAL INFORMATION SERVICE (NTIS), SPRINGFIELD, VA 22161.

14. NUMBER OF PRINTED PAGES

55

15. PRICE

A04

ELECTRONIC FORM



